

Cite this: *Polym. Chem.*, 2025, **16**, 2784

## Synthesis and depolymerization studies of biohybrid polycarbonates derived from terpenes†

Thirusangumurugan Senthamarai,<sup>a</sup> Enrico Lanaro,<sup>id a,b</sup> Jack Tinker,<sup>id c</sup> Antoine Buchard<sup>id c</sup> and Arjan W. Kleij<sup>id \*a,d</sup>

We here report the catalytic ring-opening copolymerization of 2-menthene oxide (**MO**), a terpene-based monomer derived from *L*-menthol, and CO<sub>2</sub> to provide poly(menthene carbonate), **PMC**, with a maximum molecular weight (*M<sub>n</sub>*) of 10.2 kg mol<sup>-1</sup>. The terpene monomer **MO** can also be combined with both limonene oxide (**LO**) and CO<sub>2</sub> 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**/CO<sub>2</sub> or **LO**/CO<sub>2</sub>, 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.

Received 20th March 2025,  
Accepted 2nd May 2025

DOI: 10.1039/d5py00285k

rsc.li/polymers

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.<sup>1–5</sup> 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.<sup>6,7</sup> The safe disposal and reuse of commercial PC is, however, complicated by toxicity concerns of BPA metabolites.<sup>8</sup> Furthermore, the commercial PC production process makes use of diphenylcarbonate (DPC) as a carbonylating agent.<sup>9</sup> 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 CO<sub>2</sub> is intrinsically a much safer alternative to prepare polycarbonates and at present represents the most versatile approach to produce polycarbonates.<sup>10–12</sup>

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.<sup>13–20</sup> 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.<sup>21–27</sup> 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.<sup>28–30</sup>

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.<sup>31,32</sup> As far as we are aware, the Greiner group reported the only example of the ROCOP of sterically demanding 2-menthene oxide (**MO**) and CO<sub>2</sub> to provide poly(menthene carbonate), **PMC**.<sup>33</sup> 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<sub>g</sub>* 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

<sup>a</sup>Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 – Tarragona, Spain.

E-mail: akleij@iciq.es

<sup>b</sup>Departament de Química Física i Inorgànica/Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 – Tarragona, Spain<sup>c</sup>Green Chemistry Centre of Excellence, Department of Chemistry, University of York, YO10 5DD York, UK<sup>d</sup>Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 – Barcelona, Spain† Electronic supplementary information (ESI) available: Experimental details, characterization data for all monomers and polycarbonates, and copies of relevant spectra and chromatograms. See DOI: <https://doi.org/10.1039/d5py00285k>

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.<sup>27,34</sup> 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<sup>31,32,35</sup> we attained with the copolymerization of limonene oxide (**LO**) and CO<sub>2</sub> 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 CO<sub>2</sub> (Table 1) promoted by the Al(III) complex **Al<sup>Me</sup>** and PPNCI (Table 1; PPN = bis(triphenyl)iminium).

The copolymerization of both **LO** and **MO** with CO<sub>2</sub> and promoted by **Al<sup>Me</sup>**/PPNCI 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 CO<sub>2</sub> ( $M_n = 6.84 \text{ kg mol}^{-1}$ ). 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  $4.89 \text{ kg mol}^{-1}$  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 CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub> catalyzed by **Al<sup>Me</sup>**/PPNCI<sup>a</sup>



Entry	<b>LO</b> : <b>MO</b>	Solv.	$T/t^b$	Conv. <sup>c</sup> (%)	$m:n^d$	$M_n/D^e$
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 <sup>f</sup>	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 <sup>g</sup>	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 <sup>f</sup>	1:1	—	45, 72	71	64:36	8.87, 1.25
18 <sup>g</sup>	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

<sup>a</sup> Reaction conditions: **MO**:**LO** (6.5 mmol) ratio as indicated, **Al<sup>Me</sup>** (1 mol%) and PPNCI (0.5 mol%), toluene (0.5 M), 15 bar CO<sub>2</sub>, 45 °C, 72 h. <sup>b</sup>  $T$  denotes the reaction temperature in °C and  $t$  is the reaction time in h. <sup>c</sup> Values correspond to the overall epoxide conversion as determined by <sup>1</sup>H NMR (CDCl<sub>3</sub>). <sup>d</sup> Determined by <sup>1</sup>H NMR (CDCl<sub>3</sub>) using the signal integrals of the methine hydrogens of the **LO** and **MO** based repeat units. <sup>e</sup>  $M_n$  values are given in kg mol<sup>-1</sup> and  $D = M_w/M_n$ , all values determined by GPC in THF calibrated with polystyrene standards. <sup>f</sup> Carried out at 30 bar CO<sub>2</sub> pressure. <sup>g</sup> Using 0.5 mol% **Al<sup>Me</sup>** and 0.25 mol% PPNCI. For the majority of the experiments done, the theoretical mass of the polycarbonates using 1 mol% of **Al<sup>Me</sup>** is approximately  $19.7 \text{ kg mol}^{-1}$  with **MO** and **LO** having nearly the same molar mass (154.25 *vs.* 152.24 g mol<sup>-1</sup>). The carbonate selectivity for all polymers was >95% as evidenced by <sup>1</sup>H NMR.

these conditions the propagation rate would be lower due to a higher dilution of both catalyst components leading to lower epoxide conversion.<sup>36</sup> 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  $\text{CO}_2$ , 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  $10.2 \text{ kg mol}^{-1}$  (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  $\text{CO}_2$  pressure was also successful (entry 17) though the **PLMC** product had a slightly lower  $M_n$  of  $8.87 \text{ kg mol}^{-1}$ . 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  $\text{CO}_2$ -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†).<sup>28,29</sup> 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<sup>a</sup>



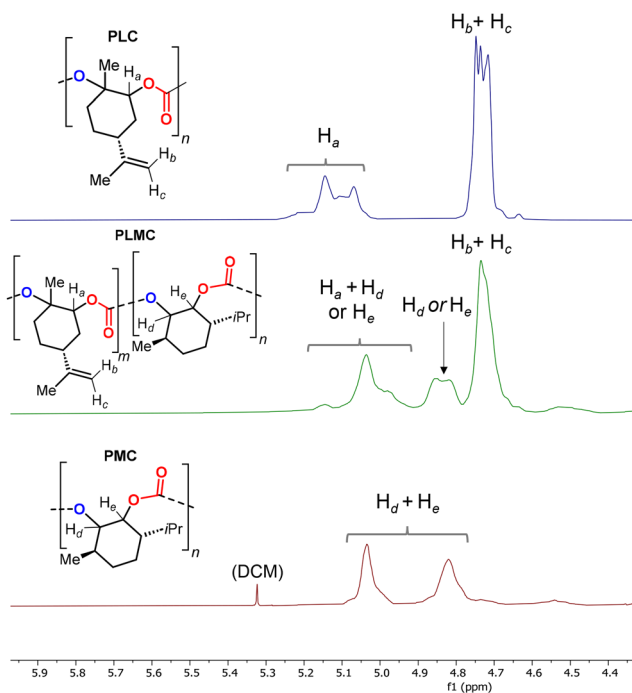
Entry	P	t, TBD	m : n <sup>b</sup>	Conv. <sup>c</sup> (%)	Sel. <sup>d</sup> (%)	m : n <sup>c</sup>
1	<b>P1</b>	24, 4	65 : 35	27	44	61 : 39
2	<b>P1</b>	15, 8	65 : 35	87	79	87 : 13
3	<b>P1</b>	15, 12	65 : 35	93	70	83 : 17
4	<b>P1</b>	15, 16	65 : 35	>98	98	66 : 34
5 <sup>e</sup>	<b>P1</b>	15, 12	65 : 35	>98	93	66 : 34
6 <sup>f</sup>	<b>P1</b>	15, 11	65 : 35	>98	>98	59 : 41
7 <sup>f</sup>	<b>P2</b>	15, 11	85 : 15	>98	>98	83 : 17
8 <sup>f</sup>	<b>P3</b>	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:**  $M_n = 7.92 \text{ Kg/mol}$ ,  $D = 1.21$ ;  $m:n = 57:43$

<sup>a</sup> Reaction conditions: polycarbonate (100 mg), toluene (0.5 mL), 15 h, 111 °C. <sup>b</sup> Values for the starting polymer as determined by  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ). <sup>c</sup> Determined by  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) of the depolymerized polymer sample. <sup>d</sup> Total epoxide selectivity, the remaining products were the cyclic carbonates. <sup>e</sup> The solvent was  $\text{CH}_3\text{CN}$ . <sup>f</sup> The solvent was  $\text{CH}_3\text{CN}$  (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 3** Functionalization of the C=C bonds in PLC and a hybrid polycarbonate<sup>a</sup>


Data ↓	PLC	PLC <sup>S</sup>	PLMC	PLMC <sup>S</sup>
$M_n$ (kg mol <sup>-1</sup> ) <sup>b</sup>	7.8	13.2	10.2	16.2
$D^b$	1.38	1.32	1.28	1.21
% C=C <sup>c</sup>	>99	<5	65	<4
IR (cm <sup>-1</sup> ) <sup>d</sup>	1742 <sup>e</sup>	1744	1744	1746
$T_g$ (°C) <sup>f</sup>	104	-25 <sup>g</sup>	109 <sup>g</sup>	13 <sup>g</sup>
$T_d^{10}$ (°C) <sup>h</sup>	217	265	237	269
Appearance <sup>i</sup>	Solid	Oil	Solid	Oil

<sup>a</sup> Reaction conditions: thiol-to-double bond ratio was 2 : 1, 70 °C, 18 h. <sup>b</sup>  $M_n$  and  $D$  values were determined by GPC in THF calibrated with polystyrene standards, a previously prepared sample of PLC was utilized. <sup>c</sup> As determined by <sup>1</sup>H NMR spectroscopy (CDCl<sub>3</sub>) using the signal integrals of the remaining C=C hydrogens *versus* the methine-H; data refer to the C=C bonds present in the entire polymer product. <sup>d</sup> Carbonate absorbance. <sup>e</sup> Taken from ref. 31. <sup>f</sup> Data collected by differential scanning calorimetry (DSC), the data refer to the second heating. <sup>g</sup> The value represents a  $T_m$  (melting point). <sup>h</sup> Measured by thermogravimetric analysis (TGA) using the  $T_d$  value at 5% weight loss. <sup>i</sup> Oil here refers to a transparent, highly viscous material.

semi-crystalline behavior was noted for these hybrid PCs (see the ESI, see section 5 and Fig. S7–S21†). We wondered whether we could use the C=C double bonds present in the LO-based repeat units to manipulate their processability features. Thereto, we used a thiol-ene approach to functionalize the olefinic fragments present in both PLC and PLMC (entry 13, Table 1 and ESI, Fig. S12, S15 and S21†). Radical initiated functionalization by a C<sub>12</sub>-derived thiol proved to both efficient and easy allowing to convert >95% of the C=C bonds (supported by <sup>1</sup>H NMR analysis and a substantial increase in  $M_n$  as measured by GPC) in both samples to their respective polythioether derivatives. While both PLC and PLMC are white solids, the appearance of their functionalized counterparts (PLC<sup>S</sup> and PLMC<sup>S</sup>) was quite different being highly viscous and oily in nature. This indicated that the functionalization process significantly altered their initial thermal behavior. Indeed, upon analysis by DSC, clear melting and crystallization temperatures ( $T_m$  and  $T_c$ ) were observed. For both PLC<sup>S</sup> ( $T_m$  = -25 °C, with  $T_c$  = -39 °C) and PLMC<sup>S</sup> ( $T_m$  = +13 °C, with a  $T_c$  of -47 °C, see Fig. 2 and the ESI, Fig. S12 and S21†) these temperatures are significantly below ambient conditions, and clearly show that the introduction of the long tail alkyl groups increases the molecular ordering in these macromolecules most likely being the result of substantial intertwining. TGA analyses showed that the functionalization process resulted in materials with higher decomposition temperatures ( $T_d^{10}$ ) at least 30 °C higher than the non-functionalized polymers.

**Fig. 2** DSC analysis of PLC<sup>S</sup>, note that the data refer to the second heating/cooling.

We then sought to extend the types of monomers that can be used to create bio-hybrid polycarbonates (Table 4). The originally used monomers MO and LO were combined with either an acyclic terpene oxide derived from *O*-protected citronellol (abbreviated as CO) or a sugar-derived oxetane (OX).<sup>26,27,34</sup> First the copolymerization of CO with CO<sub>2</sub> was attempted but the low conversion of CO (entry 1, 20%; P4,  $M_n$  = 1.34 kg mol<sup>-1</sup>) after three days was a testament to the more difficult nature of the coupling between acyclic trisubstituted terpene oxides and CO<sub>2</sub>.<sup>37</sup> In the presence of LO or MO, terpolymers P5 (entry 2;  $M_n$  = 4.62 kg mol<sup>-1</sup>) and P6 (entry 3;  $M_n$  = 2.26 kg mol<sup>-1</sup>) were formed, respectively, with low CO-incorporation levels of around 10%. This reconfirms the sluggish nature of the monomer CO. We then shifted our focus to bicyclic xylose-based OX (entries 4–8). At 70 °C, the copolymerization of OX with CO<sub>2</sub> under Al<sup>Me</sup>/PPNCl catalysis affords only oligomeric P7 (entry 4;  $M_n$  = 1.51 kg mol<sup>-1</sup>) at a low OX conversion (10%). Raising the reaction temperature to 100 °C (entry 5) allowed to increase both the OX conversion (to 85%) and the molecular weight of the oligomer P7 formed ( $M_n$  = 4.28 kg mol<sup>-1</sup>).

Then, monomers LO and OX were combined under the optimized conditions of Table 1 (entry 13; with  $T$  = 50 °C)<sup>38</sup> showing only a very modest monomer conversion of 14% (Table 4, entry 6). The oligomeric carbonate that had formed (P8) only had the LO monomer incorporated representing thus a co-instead of the targeted terpolymer ( $m:n > 99:1$ ). Under these conditions the OX monomer remained unaffected and could not be activated.

Next, we examined a ternary combination of MO, OX and CO<sub>2</sub> (entries 7 and 8) to give access to P9. At 65 °C and 15 bar CO<sub>2</sub> pressure (entry 7), the presence of binary system Al<sup>Me</sup>/PPNCl again only afforded an oligomeric carbonate P9 at low MO conversion (20%) with no observable incorporation of OX. When increasing the reaction temperature to 100 °C, effective



**Table 4** Co- and terpolymerization reactions using **MO**, **LO**, **CO** or **OX** with  $\text{CO}_2$  catalyzed by  $\text{Al}^{\text{Me}}/\text{PPNCl}^{\text{a}}$ 

$\text{cyclic ether monomer(s)} \xrightarrow[\text{solvent/heat}]{\text{Al}^{\text{Me}}/\text{PPNCl}^{\text{cat}}, \text{CO}_2, \text{T}, \text{t}}$

**P4:** CO/ $\text{CO}_2$   
**P5:** LO/ $\text{CO}/\text{CO}_2$   
**P6:** MO/ $\text{CO}/\text{CO}_2$   
**P7:** OX/ $\text{CO}_2$   
**P8:** LO/OX/ $\text{CO}_2$   
**P9:** MO/OX/ $\text{CO}_2$

**Al<sup>Me</sup>**  
**PPNCl**  
**LO**    **MO**    **CO**    **OX**

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

<sup>a</sup> Reaction conditions: monomer ratio 1 : 1 (where applicable), neat, 65 °C, 15 bar  $\text{CO}_2$ , 72 h. <sup>b</sup> Values correspond to the overall epoxide conversion as determined by  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ ). <sup>c</sup> Determined by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) using the signal integrals of the methine hydrogens of the **LO** and **MO** based repeat units. <sup>d</sup>  $M_n$  values are given in  $\text{kg mol}^{-1}$  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. <sup>e</sup> Reaction was performed at 50 °C. <sup>f</sup> Reaction was performed at 70 °C for 48 h using 2.9 mmol of **OX** in toluene as a medium. <sup>g</sup> Reaction was performed at 100° and 20 bar  $\text{CO}_2$  pressure for 72 h using 2.9 mmol of **OX** in toluene (0.25 M) as a medium. <sup>h</sup> Conversion refers to **OX**, the conversion of **MO** was <5%.

activation of **OX** takes place (96% conversion as measured by  $^1\text{H}$  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 polycarbo-

nates 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 $\text{CO}_2$

Inside a glove box, a 50 mL autoclave was charged with complex  $\text{Al}^{\text{Me}}$  (33.0 mg, 65.7  $\mu\text{mol}$ , 0.01 equiv.) and **PPNCl** (18.3 mg, 32.8  $\mu\text{mol}$ , 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  $\text{CO}_2$ . 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  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 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  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ ), taking small aliquots from the reactive mixture. At the end of the reaction, the crude product was analyzed by  $^1\text{H}$  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.

## Acknowledgements

We thank the Cerca program/Generalitat de Catalonia, ICREA, MICINN (PID2020-112684GB-I00, PID2023-149295NB-I00 and Severo Ochoa Excellence Accreditation 2020–2023 CEX2019-000925-S) and AGAUR (2021-SGR-00853) for financial support. TS is thankful to European Union's Horizon 2020 research and innovation program for a Marie Skłodowska-Curie grant (101110356), and EL acknowledges financial support from the European Union (Marie Skłodowska-Curie Grant Agreement No. 101073223, D-Carbonize project). Research funding from the Royal Society (URF\R\221027: fellowship to AB and studentship to JT) is also acknowledged.

## References

- 1 J.-G. Rosenboom, R. Langer and G. Traverso, Bioplastics for a circular economy, *Nat. Rev. Mater.*, 2022, 7, 117–137.
- 2 C. Veith, F. Diot-Néant and S. A. Miller, Synthesis and polymerization of bio-based acrylates: a review, *Polym. Chem.*, 2020, 11, 7452–7470.
- 3 T. O. Machado, C. J. Stubbs, V. Chiaradia, M. A. Alraddadi, A. Brandolese, J. C. Worch and A. P. Dove, A renewably sourced, circular photopolymer resin for additive manufacturing, *Nature*, 2024, 629, 1069–1074.
- 4 C. J. Stubbs, J. C. Worch, H. Prydderch, Z. Wang, R. T. Mathers, A. V. Dobrynin, M. L. Becker and A. P. Dove, Sugar-Based Polymers with Stereochemistry-Dependent Degradability and Mechanical Properties, *J. Am. Chem. Soc.*, 2022, 144, 1243–1250.
- 5 R. M. Cywar, N. A. Rorrer, C. B. Hoyt, G. T. Beckham and E. Y.-X. Chen, Bio-Based Polymers with Performance-Advantaged Properties, *Nat. Rev. Mater.*, 2022, 7, 83–103.
- 6 M. Karhankova, A. Mizera, M. Adamek, V. Mach, P. Stoklasek and M. Gracla, Mechanical resistance of safety

elements in transportation, *Transp. Res. Proc.*, 2023, 74, 732–739.

- 7 A. L. De la Colina Martínez, G. Martínez Barrera, C. E. Barrera Díaz, L. I. Ávila Córdoba, F. Ureña Núñez and D. J. Delgado Hernández, Recycled polycarbonate from electronic waste and its use in concrete: Effect of irradiation, *Constr. Build. Mater.*, 2019, 201, 778–785.
- 8 Y. Ma, H. Liu, J. Wu, L. Yuan, Y. Wang, X. Du, R. Wang, M. Marwa, P. Petlulu, X. Chen and H. Zhang, The adverse health effects of bisphenol A and related toxicity mechanisms, *Environ. Res.*, 2019, 176, 108575.
- 9 For details on the use of DPC consult: <https://cdn.intratec.us/docs/reports/previews/pc-e21a-b.pdf>.
- 10 S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Sainia and C. K. Williams, Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates, *Chem. Commun.*, 2015, 51, 6459–6479.
- 11 C. A. L. Lidston, S. M. Severson, B. A. Abel and G. W. Coates, Multifunctional Catalysts for Ring-Opening Copolymerizations, *ACS Catal.*, 2022, 12, 11037–11070.
- 12 X. Xie, Z. Huo, E. Jang and R. Tong, Recent advances in enantioselective ring-opening polymerization and copolymerization, *Commun. Chem.*, 2023, 6, 202.
- 13 G.-P. Wu, P.-X. Xu, X.-B. Lu, Y.-P. Zu, S.-H. Wei, W.-M. Ren and D. J. Darensbourg, Crystalline CO<sub>2</sub> Copolymer from Epichlorohydrin via Co(III)-Complex-Mediated Stereospecific Polymerization, *Macromolecules*, 2013, 46, 2128–2133.
- 14 G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, B. Li, Y.-P. Zu and D. J. Darensbourg, Alternating Copolymerization of CO<sub>2</sub> and Styrene Oxide with Co(III)-Based Catalyst Systems: Differences Between Styrene Oxide and Propylene Oxide in Reactivity, Polymer Selectivity, and Regioselective Ring-Opening, *Energy Environ. Sci.*, 2011, 4, 5084–5092.
- 15 D. J. Darensbourg and S. J. Wilson, The Synthesis of Poly(indene carbonate) from Indene Oxide and Carbon Dioxide—A Polycarbonate with a Rigid Backbone, *J. Am. Chem. Soc.*, 2011, 133, 18610–18613.
- 16 W. C. Ellis, Y. Jung, M. Mulzer, R. Di Girolamo, E. B. Lobkovsky and G. W. Coates, Copolymerization of CO<sub>2</sub> and meso Epoxides Using Enantioselective β-Diiminate Catalysts: A Route to Highly Isotactic Polycarbonates, *Chem. Sci.*, 2014, 5, 4004–4011.
- 17 J. G. Kim and G. W. Coates, Synthesis and Polymerization of Norbornenyl-Terminated Multiblock Poly(cyclohexene carbonate)s: A Consecutive Ring-Opening Polymerization Route to Multisegmented Graft Polycarbonates, *Macromolecules*, 2012, 45, 7878–7883.
- 18 M. Winkler, C. Romain, M. A. R. Meier and C. K. Williams, Renewable Polycarbonates and Polyesters from 1,4-Cyclohexadiene, *Green Chem.*, 2015, 17, 300–306.
- 19 T. M. McGuire, A. C. Deacy, A. Buchard and C. K. Williams, Solid-State Chemical Recycling of Polycarbonates to Epoxides and Carbon Dioxide Using a Heterodinuclear Mg(II)Co(II) Catalyst, *J. Am. Chem. Soc.*, 2022, 144, 18444–18449.



- 20 C. Martín and A. W. Kleij, Terpolymers derived from Limonene Oxide and Carbon Dioxide: Access to Cross-Linked Polycarbonates with Improved Thermal Properties, *Macromolecules*, 2016, **49**, 6285–6295.
- 21 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, Bio-Based Polycarbonate from Limonene Oxide and CO<sub>2</sub> with High Molecular Weight, Excellent Thermal Resistance, Hardness and Transparency, *Green Chem.*, 2016, **18**, 760–770.
- 22 V. Bonamigo Moreira, J. Rintjema, F. Bravo, A. W. Kleij, L. Franco, J. Puiggalí, C. Alemán and E. Armelin, Novel Biobased Epoxy Thermosets and Coatings from Poly (Limonene Carbonate) Oxide and Synthetic Hardeners, *ACS Sustainable Chem. Eng.*, 2022, **10**, 2708–2719.
- 23 O. Hauenstein, S. Agarwal and A. Greiner, Bio-Based Polycarbonate as Synthetic Toolbox, *Nat. Commun.*, 2016, **7**, 11862.
- 24 T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. E. Koning, Bio-derived Polymers for Coating Applications: Comparing Poly (Limonene Carbonate) and Poly(Cyclohexadiene Carbonate), *Polym. Chem.*, 2017, **8**, 6099–6105.
- 25 S. Reiter, A. Vagin, C. Kronast, B. Jandl and B. Rieger, Lewis Acid  $\beta$ -Diiminato-Zinc-Complex as All-rounder for Co- and Terpolymerisation of various Epoxides with Carbon Dioxide, *Chem. Sci.*, 2017, **8**, 1876–1882.
- 26 T. M. McGuire and A. Buchard, Polymers from Sugars and CS<sub>2</sub>: Ring Opening Copolymerisation of a D-xylose Anhydrosugar Oxetane, *Polym. Chem.*, 2021, **12**, 4253.
- 27 D. K. Tran, A. Z. Rashad, D. J. Darensbourg and K. L. Wooley, Sustainable Synthesis of CO<sub>2</sub>-derived Polycarbonates from D-xylose, *Polym. Chem.*, 2021, **12**, 5271.
- 28 C. Li, R. J. Sablong, R. A. T. M. van Benthem and C. E. Koning, Unique Base-Initiated Depolymerization of Limonene-Derived Polycarbonates, *ACS Macro Lett.*, 2017, **6**, 684–688.
- 29 D. H. Lamparelli, A. Villar-Yanez, L. Dittrich, J. Rintjema, F. Bravo, C. Bo and A. W. Kleij, Bicyclic Guanidine Promoted Mechanistically Divergent Depolymerization and Recycling of a Biobased Polycarbonate, *Angew. Chem., Int. Ed.*, 2023, **62**, e202314659.
- 30 F. N. Singer, A. C. Deacy, T. M. McGuire, C. K. Williams and A. Buchard, Chemical Recycling of Poly(Cyclohexene Carbonate) Using a Di-MgII Catalyst, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201785.
- 31 L. Peña Carrodeguas, J. González-Fabra, F. Castro-Gómez, C. Bo and A. W. Kleij, AlIII-Catalysed Formation of Poly (limonene)-carbonate: DFT Analysis of the Origin of Stereoregularity, *Chem. – Eur. J.*, 2015, **21**, 6115–6122.
- 32 N. Kindermann, À. Cristófol and A. W. Kleij, Access to Biorenewable Polycarbonates with Unusual Glass-Transition Temperature ( $T_g$ ) Modulation, *ACS Catal.*, 2017, **7**, 3860–3863.
- 33 A. Wambach, S. Agarwal and A. Greiner, Synthesis of Biobased Polycarbonate by Copolymerization of Menth-2-ene Oxide and CO<sub>2</sub> with Exceptional Thermal Stability, *ACS Sustainable Chem. Eng.*, 2020, **8**, 14690–11469.
- 34 T. M. McGuire, J. Bowles, E. Deane, E. H. E. Farrar, M. N. Grayson and A. Buchard, Control of Crystallinity and Stereocomplexation of Synthetic Carbohydrate Colymers from d- and l-xylose, *Angew. Chem., Int. Ed.*, 2021, **60**, 4524–4528.
- 35 A. Brandolese and A. W. Kleij, Catalyst Engineering Empowers the Creation of Biomass-Derived Polyesters and Polycarbonates, *Acc. Chem. Res.*, 2022, **55**, 1634–1645.
- 36 The observation of lower molecular weight polycarbonates with similar types of binary catalysts using biobased epoxide monomer has been observed in other cases, see: A. Brandolese, D. H. Lamparelli, I. Grimaldi, S. Impemba, P. Baglioni and A. W. Kleij, Access to Functionalized Polycarbonates derived from Fatty Acid Esters via Catalytic ROCOP and their Potential in Gel Formulations, *Macromolecules*, 2024, **57**, 3816–3823, See also ref. 31 and 32.
- 37 G. Fiorani, M. Stuck, C. Martín, M. Martínez-Belmonte, E. Martín, E. C. Escudero-Adán and A. W. Kleij, Catalytic Coupling of Carbon Dioxide with Terpene Scaffolds: Access to Challenging Bio-Based Organic Carbonates, *ChemSusChem*, 2016, **9**, 1304–1311.
- 38 Note that typically the LO/CO<sub>2</sub> copolymerization using Al<sup>Me</sup>/PPNCl can be carried out at around 45 °C justifying the temperature conditions for entry 7 in Table 4, see ref. 31 and 32.

