

# High Molar Mass Polycarbonates as Closed-Loop Recyclable Thermoplastics

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**ABSTRACT:** Using carbon dioxide (CO<sub>2</sub>) to make recyclable thermoplastics could reduce greenhouse gas emissions associated with polymer manufacturing. CO<sub>2</sub>/cyclic epoxide ring-opening copolymerization (ROCOP) allows for >30 wt% of the polycarbonate to derive from CO<sub>2</sub>; so far, the field has largely focused on oligocarbonates. In contrast, efficient catalysts for high molar mass polycarbonates are under-investigated and the resulting thermoplastic structure-property relationships, processing and recycling need to be elucidated. This work describes a new organometallic Mg(II)Co(II) catalyst that combines high productivity, low loading tolerance, the highest polymerization control and yields polycarbonates with  $M_n$  values from 4–130 kg mol<sup>-1</sup>, with narrow, monomodal distributions. It is used in the ROCOP of CO<sub>2</sub> with bicyclic epoxides to produce a series of samples, each with  $M_n > 100$  kg mol<sup>-1</sup>, of poly(cyclohexene carbonate) (PCHC), poly(vinyl-cyclohexene carbonate) (PvCHC), poly(ethyl-cyclohexene carbonate) (PeCHC, by hydrogenation of PvCHC) and poly(cyclopentene carbonate) (PCPC). All these materials are amorphous thermoplastics, with high glass transition temperatures ( $85 < T_g < 126$  °C, by DSC) and high thermal stability ( $T_d > 260$  °C). The cyclic ring substituents mediate the materials' chain entanglements, viscosity, and glass transition temperatures. Specifically, PCPC was found to have 10x lower entanglement  $M_n$  and 100x lower zero-shear viscosity compared to PCHC, showing potential as a future thermoplastic. All these high molecular weight polymers are fully recyclable, either by re-processing or by using the Mg(II)Co(II) catalyst for highly selective depolymerizations to epoxides and CO<sub>2</sub>. PCPC shows the fastest depolymerization rates, achieving an activity of 2500 h<sup>-1</sup> and >99% selectivity for cyclopentene oxide and CO<sub>2</sub>.

## Introduction

Polymers are among the largest scale chemicals produced; they are currently manufactured at a rate of around 400 megatonnes (Mt) annually.<sup>1–3</sup> Their production from petrochemicals accounts for >1.0 gigatonne of carbon dioxide-equivalents (Gt CO<sub>2</sub>-equiv.), representing >60% of overall lifecycle emissions. The total carbon footprint and other environmental pollution is exacerbated by a lack of effective recycling.<sup>3–5</sup> Two important strategies to address these issues have emerged from several recent, independent global plastics systemic models: (1) replace virgin petrochemical feedstocks with carbon dioxide utilization technologies (CCU), either directly achieved by CO<sub>2</sub>-based chemistries or through biomass upgrading; and (2) drastically increase thermoplastic recycling rates, ensuring all future materials undergo energy efficient mechanical recycling and/or chemical recycling to monomers.<sup>1–2, 6–10</sup> Our interest is to produce polycarbonate thermoplastics, directly using CO<sub>2</sub>, showing useful properties and selective end-life recycling (both mechanical and chemical).<sup>7–9</sup>

CO<sub>2</sub> and epoxide ring-opening copolymerization (ROCOP) is a front-runner carbon dioxide utilization technology.<sup>11–13</sup> Most polymerizations apply catalysts to produce hydroxyl telechelic oligocarbonates ( $1 < M_n < 20$  kg mol<sup>-1</sup>), or CO<sub>2</sub>-polyols, which are important as surfactants and in production of polyurethane foams, elastomers, coatings, sealants and adhesives.<sup>13–18</sup> Some excellent catalysts include Co(III) or Al(III) complexes tethered to ionic co-catalysts (often bis(triphenylphosphine)iminium halides, e.g. PPNCl); dimeric/dinuclear complexes, e.g. Zn(II)Zn(II), Zn(II)Mg(II), Co(II)Mg(II), Ln(III)Zn(II), which operate without any co-catalyst; or borane complexes tethered to/used with ionic co-catalysts (ammonium or phosphonium halides).<sup>19–41</sup> Such CO<sub>2</sub>-polyol catalysts need to be applied with a very large-excess (10–100 equivalents vs. catalyst) of a protic chain transfer agent (CTA), often a diol, which controls the oligomer chain length and hydroxyl chain end-groups.<sup>42</sup> Chain transfer reactions are alcoholysis processes, whereby all alcohol groups react rapidly with the growing polymer chains, moving them rapidly on/off the catalyst; these processes generally occur faster than propagation.<sup>27, 43–44</sup>

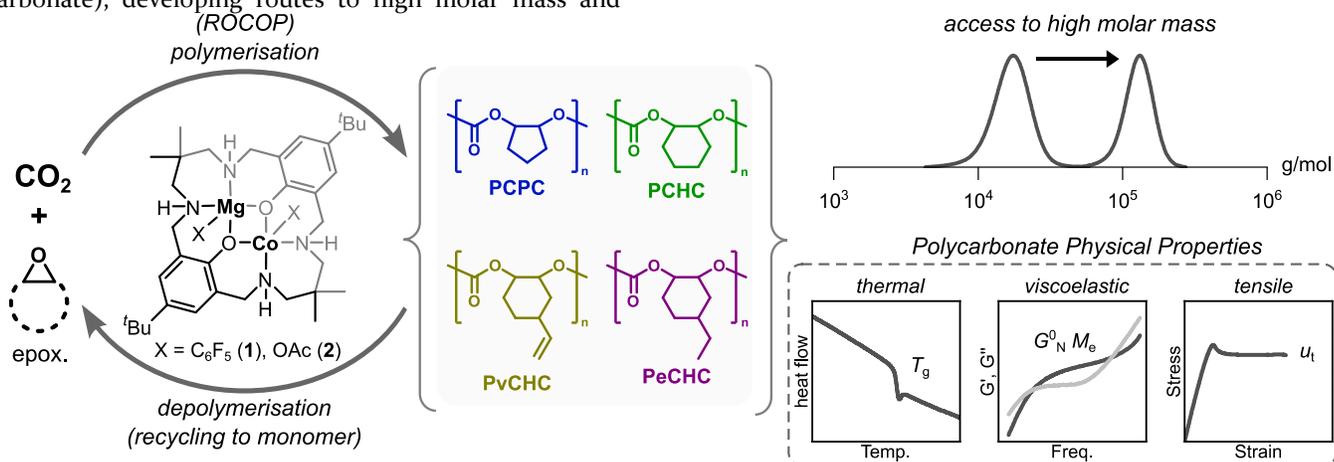
Most catalysts also react with residual water, either in the apparatus or monomers, to ring-open epoxides and generate diols *in-situ* which are also bifunctional CTAs. With the inclusion of these added (or inadvertent) mono- and bi-functional CTAs, together with catalysts or co-catalysts featuring a monofunctional initiator (usually an acetate or chloride), the polymer molar masses almost inevitably exhibit bimodal distributions.<sup>42, 44</sup> These restrictions on molar masses, where the  $M_n$  is well below the entanglement molecular weight ( $M_e$ ), and high dispersities ( $\mathcal{D}$ ) have so far hampered CO<sub>2</sub>-based polymers from effectively challenging petroleum-based commodity thermoplastics. For instance, prior studies of poly(cyclohexene carbonate) (PCHC) have consistently noted its difficult processability and high brittleness.<sup>45-46</sup>

In contrast, catalysts that yield high molar mass polycarbonates ( $M_n = 50\text{--}150 \text{ kg mol}^{-1}$ ) with narrow, monomodal molar mass distributions are much less common.<sup>38, 47-49</sup> Accessing such materials is desirable since entanglement phenomena directly impact many polymer physical properties, including glass transition temperature ( $T_g$ ), crystallization, mechanical strength, and processability.<sup>50</sup> In 2001, Darensbourg and Koning, reported upon a moderate molar mass PCHC sample ( $M_n = 42 \text{ kg mol}^{-1}$ ,  $M_w = 252 \text{ kg mol}^{-1}$ ,  $\mathcal{D} = 6$ ), produced using a Zn(II)Zn(II) catalyst, that showed a tensile stress of 43 MPa, Young's Modulus of 3.3 GPa, but only 2% elongation at break.<sup>45</sup> The authors estimated the entanglement molar mass to be  $\sim 15 \text{ kg mol}^{-1}$  but noted it was likely an underestimation. In 2022, Frey and Floudas investigated, both experimentally and computationally, the chain dynamics of moderate molar mass PCHC ( $5 < M_n < 33 \text{ kg mol}^{-1}$ ) produced using a [(*R,R*-salcy)CoCl]/PPNCl catalyst system, estimating an  $M_e$  of  $16 \text{ kg mol}^{-1}$ .<sup>46</sup> It is also relevant to note that PCHC has been successfully applied as a 'rigid' block in various phase separated copolymers ( $T_g$  of PCHC  $\sim 110\text{--}120 \text{ }^\circ\text{C}$ ), producing adhesives, elastomers and plastics, depending on the co-monomers and overall molar mass values.<sup>15, 18, 43, 51-53</sup> Beyond CHO as co-monomer in ROCOP, the teams of Rieger and Greiner independently focused on related 6-membered ring, bio-based poly(limonene carbonate), developing routes to high molar mass and

terpolymers with PCHC.<sup>54-56</sup> Wu and co-workers reported poly(cyclopentene carbonate) (PCPC) showed molar mass up to  $84 \text{ kg mol}^{-1}$ , but the analyzed sample ( $M_n = 20 \text{ kg mol}^{-1}$ ,  $T_g = 70 \text{ }^\circ\text{C}$ ) displayed moderate tensile strength (20 MPa) and no yield point.<sup>48</sup>

Underpinning future progress on CO<sub>2</sub>-based polycarbonates should be informed upon comprehensive material investigations, for instance by determining the  $M_e$  more accurately. To increase molar mass, two approaches to synthesize PCHC have been proposed. One consists of attempting to rigorously remove all residual protic impurities and traces of water with highly reactive scavengers; however, such purifications might be rather challenging to scale.<sup>47</sup> For instance, Jia and co-workers discovered highly active borane/PPNCl catalysts for CHO/CO<sub>2</sub> ROCOP, which when applied with rigorously dried CO<sub>2</sub> and extensively purified CHO produced PCHC with  $M_n \sim 450 \text{ kg mol}^{-1}$  ( $\mathcal{D} = 1.31$ ).<sup>47</sup> In 2022, Li and co-workers applied the same triethyl borane with different phosphazene co-catalysts to produce high molar mass PCHC ( $M_n \sim 280 \text{ kg mol}^{-1}$ ,  $\mathcal{D} = 1.59$ ).<sup>38</sup> These impressive achievements were not accompanied with material properties. A second strategy applies organometallic catalysts react *in-situ* with residual (di)ols to form only one type of initiator (the organometallic ligand does not initiate on its own).<sup>47</sup> To reach sufficient high molar masses, such catalysts must show high activity and tolerate impurities at low loadings. Previously, we reported organometallic Zn(II)Zn(II) and Zn(II)Mg(II) catalysts which exhibit such initiation control.<sup>43, 57-58</sup> Unfortunately, these catalysts were not sufficiently active to produce high molar mass polycarbonates. In 2020, we reported a very active Mg(II)Co(II) acetate catalyst for CHO/CO<sub>2</sub> ROCOP which is  $> 1000\times$  faster than Zn(II)Zn(II) and  $\sim 10\times$  faster than Mg(II)Zn(II).<sup>27</sup>

Any future uses for high molar mass CO<sub>2</sub>-based plastics must also allow for low-energy recycling options – most obviously by mechanical recycling.<sup>44</sup> In addition, chemical recycling strategies allow for recovery of the constituent monomers; in this case, epoxides and CO<sub>2</sub>.<sup>7, 59-60</sup>



**Figure 1.** Catalyst and polymers targeted in this work, with the objective of elucidating thermal-mechanical properties and recycling routes for high molar mass cyclic substituted polycarbonates.

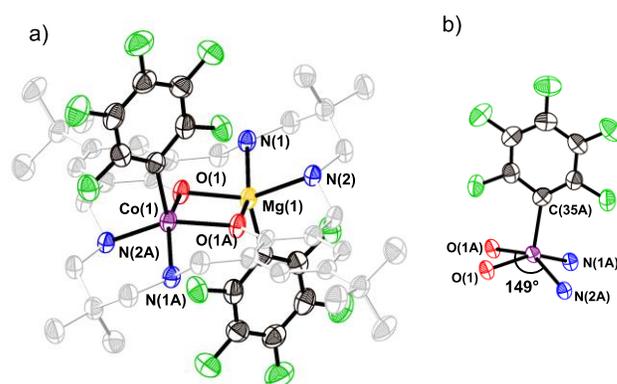
Darensbourg and co-workers pioneered CO<sub>2</sub>-derived polycarbonate chemical recycling, describing the first catalysts, applied with strong base, for the depolymerization of PCPC to cyclopentene oxide and CO<sub>2</sub>.<sup>61</sup> Subsequently, a range of other catalysts were active for PCHC and other cyclic substituted polycarbonates.<sup>62-68</sup> Although promising results have been obtained, the understanding and overall performance of such depolymerization catalysis requires improvements to maximize energy efficiency.

Thus, to address these challenges, we propose to employ a novel non-initiating organometallic Mg(II)Co(II) catalyst (Figure 1). When used with 5- and 6-membered cyclic epoxides, the latter including alkyl substituents (vinyl- and ethyl-cyclohexene), high molar mass CO<sub>2</sub>-based polycarbonates with end-group selectivity and narrow dispersity will allow us to elucidate polymer structure-property relationships. Finally, the Mg(II)Co(II) catalyst will also be investigated in depolymerization reactions, targeting high activity, selectivity, minimal catalyst loading and reducing the operating temperatures for efficient chemical recycling to high value epoxide monomer and CO<sub>2</sub>.

## Results

### Catalyst Synthesis and Carbon Dioxide ROCOP Catalysis.

To investigate the best catalysts for high molar mass polycarbonate production, the organometallic Mg(II)Co(II) complex (**1**) and previously reported Mg(II)Co(II) diacetate complex (**2**) were compared (Figure 1).<sup>27</sup> Pentafluorophenyl was selected as the organometallic ligand for its anticipated stability (with respect to  $\beta$ -H elimination), high reactivity of Co-C<sub>6</sub>F<sub>5</sub> with alcohols to undergo irreversible protonation, and low nucleophilicity of Co-C<sub>6</sub>F<sub>5</sub> to prevent CO<sub>2</sub> insertion. These features ensure that the complex is non-initiating, which is essential for high molar mass polymer production. The new organometallic Mg(II)Co(II) catalyst, **1**, was prepared with pentafluorophenyl groups as the hydrolysable non-initiating co-ligands. To make the catalyst, the macrocyclic ligand [LH<sub>2</sub>] was first reacted with [Mg{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>], followed by a reaction with cobalt(II) bis(pentafluorophenyl) ([Co(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>]) and stirring the mixture for 24 h.<sup>69-70</sup> Complex **1**, [LMgCo(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>], was isolated, by cooling the reaction solution to -30 °C, as a purple crystalline solid, in 53 % yield. Complex **2** was prepared following literature methods.<sup>27</sup> Single crystals of catalyst **1**, suitable for X-ray diffraction, were isolated *via* crystallization, from a saturated THF solution, at -30 °C. Its solid-state structure confirms the formation of a heterodinuclear complex (Figure 2a, Table S1), with the aryl co-ligands coordinated at each metal and the ligand adopting an “S” shape. In complex **1**, the Co(II) center is pentacoordinate and adopts a distorted square pyramidal geometry with the aryl ligand coordinated at the apex (Figure 2b). The Mg(II)Co(II) separation is 3.069(3) Å (Table S2 for selected bond lengths and angles).



**Figure 2.** (a) ORTEP diagram for the molecular structure of **1**. H atoms and two THF molecules have been omitted for clarity. Thermal ellipsoids at 50 % probability level. Co = purple, Mg = yellow, O = red, N = blue, F = green, C = grey (Figure S1 for full structure, Table S1 for crystallographic details). (b) Section of the crystal structure depicting the square pyramidal geometry around the cobalt center.

The <sup>1</sup>H NMR spectrum of complex **1**, in toluene-*d*<sub>8</sub>, shows peaks from -55 to 270 ppm, characteristic of a paramagnetic Co(II) species (Figure S2). Its <sup>19</sup>F{<sup>1</sup>H} NMR spectrum shows three peaks: two broad singlets at -155 ppm and -65 ppm, and a triplet at -154 ppm, the relative integrals are 2:1:1 (Figure S4, see SI for discussion on the characterization of **1**). Complex **1** was also characterized by SQUID magnetometry and cyclic voltammetry (CV). The magnetic moment, arising from the Co(II), is 4.99  $\mu_B$ , which is consistent with a square pyramidal high spin, Co(II) *d*<sup>7</sup> complex (Figure S6). Previously Hoffmann and co-workers investigated the structures for related five-coordinate Co(II) complexes and **1** shows an electronic configuration consistent with their proposal.<sup>71</sup> It also shows an irreversible Co(II/III) oxidation at  $E_{pa} = -0.819$  V (vs. Fc/Fc<sup>+</sup>), and ligand-centered oxidations at  $E_{pa} = 0.39$  V (vs. Fc/Fc<sup>+</sup>) (Figure S7).

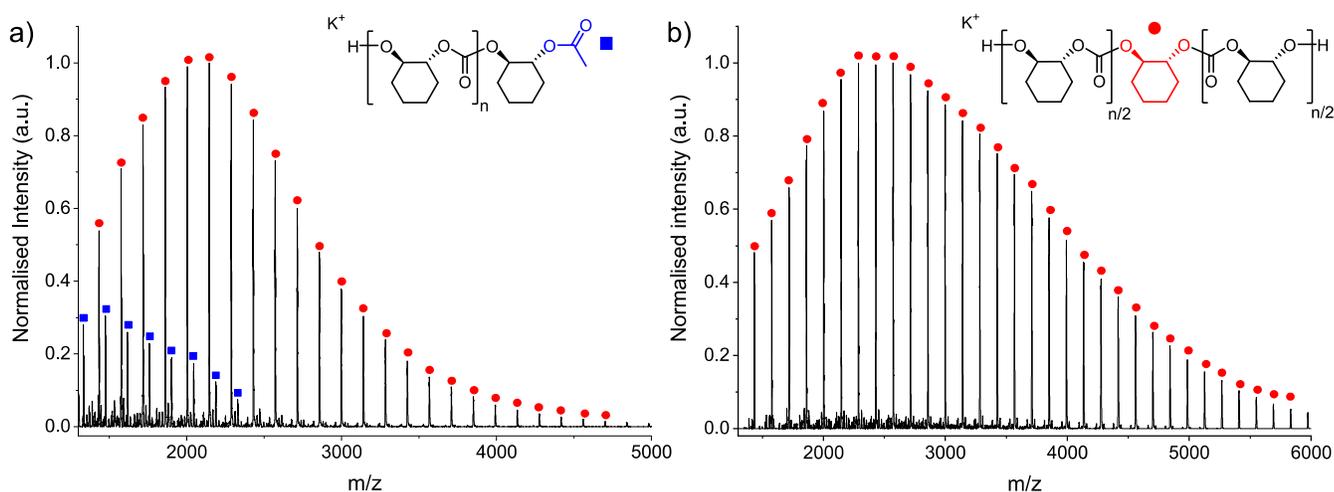
To make high molar mass polycarbonates, it is essential to cleanly control the initiation reaction and, here, this is achieved using an organometallic ligand which reacts with alcohols (CTAs). To investigate the initiation process further, complex **1** (0.01 mmol) was reacted with 2 equivalents of 2-fluorophenol at room temperature in toluene-*d*<sub>8</sub>. The reaction was conducted in a Young's tap NMR tube and monitored by spectroscopy (Figure S12). The addition of alcohol resulted in an immediate change of color, from pale to a much brighter pink (Figure S13). The resulting <sup>19</sup>F{<sup>1</sup>H} NMR spectrum showed new resonances, at -56 and -132 ppm, corresponding to the clean formation of the new 4-fluorophenoxide ligands coordinated to the Co(II) and Mg(II) centers, respectively. In addition, the product of alcoholysis, HC<sub>6</sub>F<sub>5</sub>, was also detected with 1:1 relative integration, further confirming the expected reactivity. This small-scale experiment proves that the reaction between complex **1** and alcohols is instantaneous, quantitative, and irreversible. Such reactivity is essential for initiation control during

polymerization, which is required to achieve high molar mass polymers.

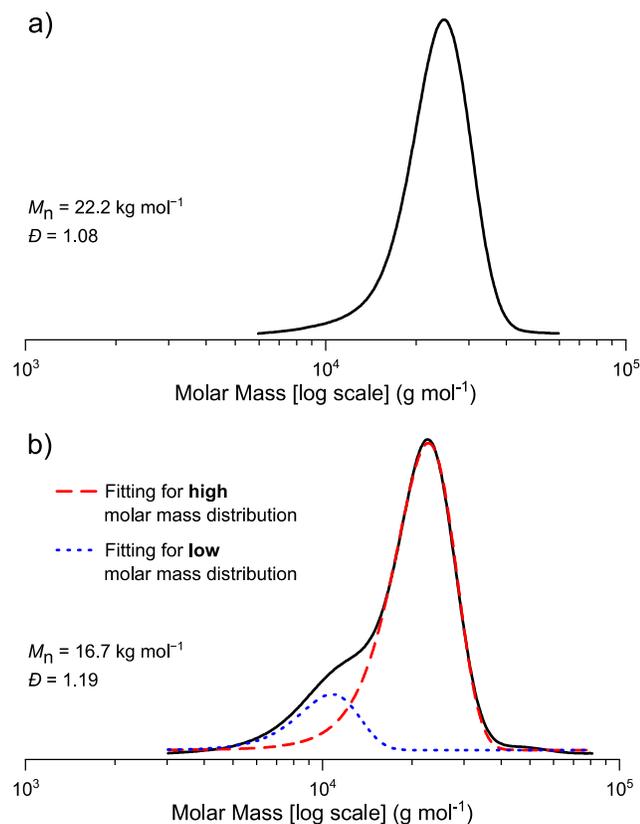
Next, the control of epoxide/CO<sub>2</sub> ROCOP with complex **1** was studied using 4 equivalents of 1,2-cyclohexane diol (CHD) as chain transfer agent and CHO as co-monomer to produce PCHC. MALDI-TOF analysis of a low molar mass PCHC sample, prepared in toluene at 80 °C using a [1]:[CHD]:[CHO] ratio of 1:4:2000, pressurized to 1 bar of CO<sub>2</sub> and quenched at low conversions (10 minutes, conv. ~5%), shows a single distribution of  $\alpha,\omega$ -dihydroxy telechelic polymer chains, initiated solely from CHD (Figure 3b). There was no evidence of any chains initiated by pentafluorophenyl groups or from carboxylates formed by carbon dioxide insertion (Figure S14 for end group calculations). In contrast, complex **2**, under identical conditions, generates polymer chains displaying both  $\alpha,\omega$ -dihydroxyl and  $\alpha$ -acetal- $\omega$ -hydroxy end-groups. The two different end-groups result from a mixture of CHD and non-innocent catalyst acetate groups, respectively (Figure 3a). Another structural feature of note is polymer tacticity, which can be determined by quantitative <sup>13</sup>C NMR spectroscopy.<sup>72</sup> The spectrum for a PCHC sample catalyzed by **1** showed that the polymer is atactic, with a Pm value of 0.5 (Figure S15).

Next, vinyl-cyclohexene oxide (vCHO)/CO<sub>2</sub> ROCOP was conducted, at 1 bar pressure, using either catalyst **1** or **2**. The vCHO co-monomer was selected since it generally polymerizes at a similar rate to CHO but benefits from an

additional alkene substituent on the cyclohexene ring which might enable post-polymerization functionalization, and enable study of pendant alkyl substituents on the dynamics of polymer chains.<sup>17, 73-76</sup> Using [1]:[CHD]:[vCHO] of 1:4:2000, at 100 °C and 1 bar of CO<sub>2</sub> pressure, the reaction reached 30% epoxide conversion within an hour and formed PvCHC with >99 % carbonate linkage selectivity (Figure S16). Catalyst **1** shows good activity, with a turn-over-frequency (TOF) of 600 h<sup>-1</sup> which is closely comparable to that using **2** (TOF = 660 h<sup>-1</sup>), under identical conditions.<sup>27</sup> Further, initial rates for these reactions, calculated from CO<sub>2</sub> mass flow data, are also very similar for catalyst **1** and **2**, with *k*<sub>obs</sub> values of 4.5 and 4.2 min<sup>-1</sup>, respectively (Figure S17). These findings demonstrate that the co-ligands (aryl or acetate) do not influence the polymerization propagation kinetics, i.e. the two catalysts feature virtually identical propagating intermediates.<sup>26, 43</sup> The ligands do, however, significantly influence the initiation processes and resulting molar masses and distributions. Using complex **1**, PvCHC has a higher molar mass and monomodal distribution (*M*<sub>n</sub> = 22.2 kg mol<sup>-1</sup>, *D* = 1.08) (Figure 4a), whilst, under identical conditions, **2** yields polymers with lower molar mass and bimodal distributions (*M*<sub>n</sub> = 16.7 kg mol<sup>-1</sup>, *D* = 1.19) (Figure 4b). In the case of complex **2**, the bimodality can be deconvoluted into a lower molar mass distribution, assigned to acetate-initiated chains, and a higher molar mass distribution, assigned to CHD-initiated polymer chains (Figure 4b).



**Figure 3.** MALDI-ToF spectra for low molar mass samples of PCHC prepared using catalysts **2** (a) or **1** (b). Polymerization conditions: [catalyst]:[CHD]:[CHO] = 1:4:2000, using a solution of 3 M CHO in toluene, 80 °C, quenched after 10 min, conv. ~5%. Chain distributions which are end-capped by CHD are marked with a red circle, and those by acetate are marked with a blue square. See Figure S14 for end group calculations and m/z peak annotation of MALDI-ToF spectra.

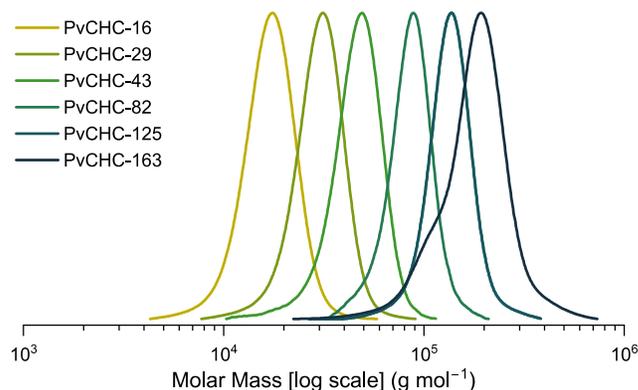


**Figure 4.** GPC traces of PvCHC (THF as eluent) produced by catalyst **1** (a) and **2** (b); in which case the molar mass peak was deconvoluted into two bimodal distributions as shown by the dashed and point lines. Polymerization conditions: [catalyst]:[CHD]:[vCHO] = 1:4:2000, 1 bar CO<sub>2</sub>, 100 °C, 1 h.

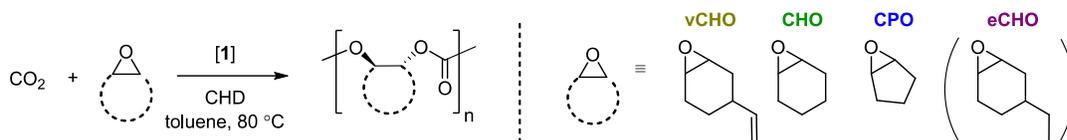
Complex **1** showed improved polymerization control and was, therefore, applied using a range of different [catalyst]:[epoxide] ratios to prepare a series of high molar mass polycarbonates. The polymerizations were all performed in toluene solutions of the appropriate epoxide (3.0 M) using steel Parr-reactors, at 20 bar CO<sub>2</sub> pressure; these conditions ensured efficient mixing and stirring particularly as conversion and viscosity increased, enabling maximum productivity (turn-over-numbers, TON) and high epoxide conversions (Table 1). It is worth noting that typical ROCOP conditions are selected to maximize polymerization rates at low epoxide conversions, where viscosities are low.<sup>77</sup> On the other hand, conditions to achieve high epoxide conversion, where viscosities are higher and rates are lower, are comparatively under-investigated. Since metal-catalyzed epoxide/CO<sub>2</sub> copolymerizations are controlled, high epoxide conversions should result in the highest polymer molar masses. Further, the polymer molar mass should be inversely related to the quantity of CHD added, since it functions as both the chain-initiator and chain-transfer agent (Figure S18). To demonstrate the outstanding polymerization control and alcohol tolerance of complex **1**, CO<sub>2</sub>/epoxide ROCOP was conducted using systematically increasing quantities of CHD (4 to 32 equivalents) vs. **1**. In these

investigations, a [1]:[vCHO] loading ratio of 1:3000 (0.033 mol% catalyst) was kept constant, and polymerizations all achieved >95% CHO conversion (Table 1, entries 1-4). Notably, the resulting series of PvCHC samples all show very narrow ( $1.07 < \bar{D} < 1.10$ ), monomodal molar mass distributions which are typical of well controlled polymerizations (Figure 5). The experimentally determined molar mass values, using GPC against polystyrene standards, are high ( $M_n$  up to 81.9 kg mol<sup>-1</sup>) and inversely related to the quantity of chain transfer agent added. The catalyst's remarkable tolerance and stability at very low concentrations and high alcohol (CHD) loadings is clear from the good correlation between experimental and theoretical molar masses,  $M_{n, est}$  (see SI for further detail). Further decreasing catalyst loadings to 0.017 mol% and even 0.010 mol%, with constant 4 equiv. of CHD, resulted in all cases in almost complete conversions (>95%) to PvCHC (Table 1, entries 5-6). These experiments yielded the target high molar masses of 125 and 163 kg mol<sup>-1</sup>, with monomodal and narrow  $\bar{D}$  (1.06–1.17) (Figure 5). The catalyst's ability to control the molar mass by varying either the catalyst or diol loading, and to achieve complete conversions, is essential to investigate the thermal-mechanical properties of the resulting materials.

Having optimized the reaction conditions to reach high molar masses with 0.010 mol% loadings of complex **1**, the ROCOP catalysis was extended using cyclohexene oxide (CHO) or cyclopentene oxide (CPO). Similarly, high epoxide conversions, at 80 °C in toluene, produced high molar mass polycarbonates (Table 1, entries 7-8). Specifically, CHO produced PCHC with  $M_n = 121.6$  kg mol<sup>-1</sup> and very narrow  $\bar{D} = 1.09$  (Figure S20); while CPO produced PCPC with  $M_n = 114.4$  kg mol<sup>-1</sup> and  $\bar{D} = 1.06$  (Figure S21). Despite these high molar masses, in these cases there are discrepancies between the experimental and theoretical values which are attributed to the use of GPC standards and/or different quantities of residual diols in the epoxides.



**Figure 5.** GPC traces (THF as eluent) of PvCHC samples produced using catalyst **1** (Table 1). A deconvoluted GPC trace of PvCHC-163 is provided in the Supporting Information (Figure S19) showing that the lower molar mass shoulder accounts for 1.2% of the total distribution.

**Table 1. Data for bicyclic epoxide/CO<sub>2</sub> ROCOP using catalyst 1.<sup>a</sup>**

Run (#)	Polymer	Epoxide	CHD equiv.	Epoxide equiv.	Time (h)	Epoxide conv. (%) <sup>b</sup>	TON <sup>c</sup>	$M_{n, GPC}$ (kg mol <sup>-1</sup> ) <sup>d</sup>	$\bar{D}$ <sup>e</sup>	$M_{n, est}$ (kg mol <sup>-1</sup> ) <sup>f</sup>
1	PvCHC-16	vCHO	32	3000	10	95	2850	16.0	1.10	14
2	PvCHC-29	vCHO	16	3000	10	99	2970	28.5	1.09	28
3	PvCHC-43	vCHO	8	3000	8	95	2850	43.4	1.10	48
4	PvCHC-82	vCHO	4	3000	10	99	2970	81.9	1.07	84
5	PvCHC-125	vCHO	4	6000	24	99	5940	124.5	1.06	126
6	PvCHC-163	vCHO	4	10,000	30	98	9800	162.8	1.17	153
7	PCHC-122	CHO	4	10,000	18	95	9500	121.6	1.09	333 <sup>g</sup>
8	PCPC-114	CPO	4	10,000	40	96	9600	114.4	1.06	320 <sup>g</sup>
9	PeCHC-125	eCHO	-	-	-	-	-	72.6	1.34	125

<sup>a</sup>Polymerizations were all conducted at 80 °C, 20 bar CO<sub>2</sub> in toluene (3 M solutions of epoxide); PeCHC was produced by hydrogenation of PvCHC (see SI for details), monomer structure shown for comparison. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy by comparing the integrals of the resonances for the epoxide vs. those of the polymer (Figure S24-S26). <sup>c</sup>TON = (moles of epoxide converted)/(moles of catalyst). <sup>d</sup>Determined by GPC, in THF, calibrated using narrow polystyrene standards. <sup>e</sup> $\bar{D} = M_w/M_n$ , determined by GPC. <sup>f</sup> $M_{n, est} = [(epoxide\ conv.)(epoxide\ equiv.)(MW\ repeat\ unit)] + [(CHD\ equiv.)(MW\ CHD)] / (CHD + x)$  (where x = residual CTA, see SI for further information). <sup>g</sup> $M_{n, est} = [(epoxide\ conv.)(epoxide\ equiv.)(MW\ repeat\ unit)] + [(CHD\ equiv.)(MW\ CHD)] / (CHD)$ .

### Hydrogenation of vinyl groups in PvCHC to PeCHC

Finally, to expand our study on the effect of ring size and substituents in CO<sub>2</sub>-derived polycarbonates, the potential to modify the alkene of PvCHC was explored. Hydrogenation of the vinyl group was selected since it will yield ethyl substituents on the cyclohexane rings - alkylated polymers are known to be more easily processed. Following a modified literature procedure, PvCHC-125 was reacted with *para*-toluenesulfonyl hydrazide and formed the corresponding alkylated polymer, PeCHC-125 in good yield (68% following repeated precipitation from MeOH).<sup>78</sup> The hydrogenation reaction did not significantly change the polymer backbone, although there was some low molar mass tailing *via* GPC ( $M_n = 72.6\text{ kg mol}^{-1}$ ,  $\bar{D} = 1.34$ ) (Figure S22-S23).

### Polycarbonate Thermal-Mechanical Properties

Any attempts to use these higher molar mass polycarbonates as thermoplastics requires insights into their thermal and viscoelastic properties since these will control the temperature ranges over which they can be processed and used. The series of ~120 kg mol<sup>-1</sup> CO<sub>2</sub>-polycarbonates were each characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and oscillatory shear rheology (Table 3). All the samples are amorphous plastics showing high glass transition temperatures ( $T_g$ ) with values, as determined by DSC, in the range 85-126 °C, and which are dependent on the ring-size and alkyl-substituents (Figure S27a). As such,

the  $T_g$  for PCHC, featuring the 6-membered ring, ( $T_{g, DSC} = 126\text{ °C}$ , which is at the limit predicted by the Fox-Flory equation),<sup>46</sup> was ~40 °C higher than for PCPC, which features the 5-membered ring, ( $T_{g, DSC} = 85\text{ °C}$ ).<sup>79</sup> Substituted rings show greater segmental motion compared to non-substituted ones, i.e., added pendant alkyl chains resulted in a slight reduction of the  $T_g$  values. Specifically, PvCHC (vinyl-substituted) and PeCHC (ethyl-substituted) showed  $T_g$  values of 118 and 105 °C, respectively, which are 8-25 °C lower than PCHC. As expected, the polymer molar mass influences the glass transition temperature, with values increasing with molar mass, e.g., PvCHC with  $M_n$  16 kg mol<sup>-1</sup> shows a glass transition temperature of 112 °C, whereas the sample with  $M_n$  82 kg mol<sup>-1</sup> shows a  $T_g$  of 118 °C (Figure S28).

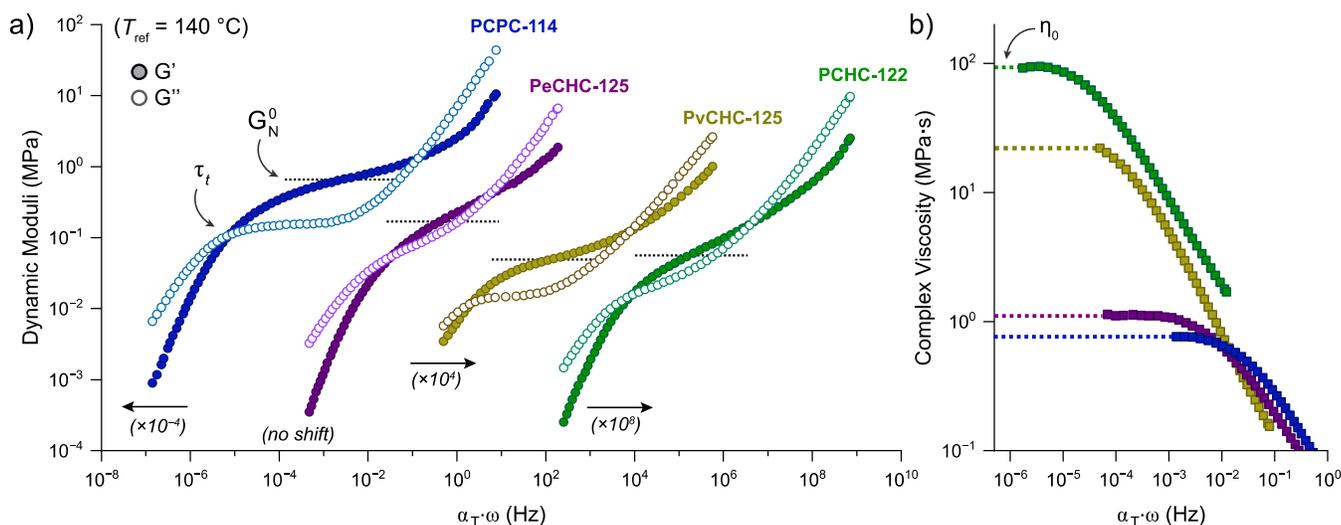
Another method to measure the glass transition temperature is from the peak in tan( $\delta$ ) obtained during variable temperature oscillatory rheology (Figures S31-S38). Analysis of the samples using this method, reveals the same trend of increasing glass transition temperatures depending on the ring sizes and pendant alkyl chains, with values increasing in the order PCPC < PeCHC < PvCHC < PCHC. Compared with those measured by DSC,  $T_g$ 's determined by rheology are all slightly higher. In addition, all polymers show the necessary high temperature stability, with the on-set of thermal decomposition occurring at temperatures ( $T_d$ ) above 265 °C (Figure S27b). These results indicate a wide processing temperature range, from 135-250 °C in all cases. It is noted that the high

temperature stability was dependent upon effective purification to remove residual catalyst, achieved by precipitation and silica-plug filtrations (see SI for details).

**Table 2. Thermal and viscoelastic properties for the high molar mass polycarbonates.<sup>a</sup>**

Polymer	$T_{g, DSC}^c$ (°C)	$T_{g, rheo}^d$ (°C)	$T_{t, cross}^e$ (°C)	$T_d^f$ (°C) <sup>b</sup>	$G'_{glass}^g$ (MPa)	$G_N^0^h$ (MPa)	$M_e^i$ (kg mol <sup>-1</sup> )	$\tau_l^j$ (min)	$\eta_0^k$ (MPa·s)
PCPC-114	85	97	166	271	453	0.65 ± 0.02	4.0–4.9	0.21 ± 0.02	0.78 ± 0.09
PeCHC-125	105	118	161	306	447	0.170 ± 0.004	15–19	0.57 ± 0.03	1.26 ± 0.11
PvCHC-125 <sup>b</sup>	118	129	196	277	459	0.049 ± 0.017	53–64	87 ± 18	30 ± 20
PCHC-122	126	132	192	265	453	0.056 ± 0.011	56	240 ± 30	90 ± 20

<sup>a</sup>Time-temperature superposition (TTS) mastercurves were referenced at 140 °C (see SI for experimental details and calculations, Figures S31–S38). <sup>b</sup>Sample was stabilised with 0.1 wt% of a radical inhibitor, pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate) (PEHC). <sup>c</sup>Measured by DSC from the second scan at a heating rate of 10 °C·min<sup>-1</sup> (Figure S27a). <sup>d</sup>Measured by oscillatory shear rheology from the peak in the tan( $\delta$ ) curve obtained during temperature ramp experiments at heating rates of 2 °C·min<sup>-1</sup> (Figures S31, S33, S35 and S37). <sup>e</sup>Terminal regime crossover temperature obtained by oscillatory shear rheology during temperature ramp experiments, 2 °C·min<sup>-1</sup>. <sup>f</sup>Onset of thermal decomposition, as measured by TGA (Figure S27b). <sup>g</sup>Low temperature glassy plateau modulus obtained by oscillatory shear rheology during temperature ramp experiments, 2 °C·min<sup>-1</sup> (Figures S31, S33, S35 and S37). <sup>h</sup>Mid-frequency rubbery plateau modulus in the TTS mastercurves (Figures S32, S34, S36 and S38). <sup>i</sup>Entanglement molecular weight, as determined from the plateau modulus,  $G_N^0$ , located at the minimum of the tan( $\delta$ ) curves in the TTS mastercurves. <sup>j</sup>Terminal relaxation time obtained as  $\tau_l = \omega^{-1}$  at which  $G' = G''$  in the TTS mastercurves. <sup>k</sup>Zero shear viscosity, obtained from the low-frequency plateau of the TTS mastercurves (Figures S32, S34, S36 and S38).



**Figure 6.** Rheological characterization of high molecular weight polycarbonates: PCPC-114 (blue), PeCHC-120 (purple), PvCHC-125 (containing 0.1 wt% of PEHC as thermal stabilizer, dark yellow), and PCHC-122 (green). (a) Plot of dynamic moduli ( $G'$  and  $G''$ ) vs. frequency (Hz), obtained from TTS master-curves (curves have been shifted horizontally for clarity, and the shift factors applied to each master-curve are specified in the plot; for unshifted TTS master-curves see SI). (b) Plot of shear viscosity vs. frequency (Hz) obtained from TTS master-curves and projection of the plateau viscosity to zero-shear.

Further insights into the polymers' molecular dynamics and extent of entanglement were obtained from the time and temperature data acquired by oscillatory shear rheology in the melt (Table 2). During temperature ramps (0.5% strain, 1.0 Hz, 2 °C·min<sup>-1</sup>), all the polycarbonates display four typical viscoelastic regions: a glassy state, a glass transition, a rubbery plateau, and the viscous flow, whose characteristic temperatures and moduli values

depend on the backbone ring size and alkyl substituents (Figures S31, S33, S35 and S37). First, only small variations were observed in the high glassy plateau moduli at the start of the oscillatory temperature investigations, with  $G' \sim 450$ – $460$  MPa. Next, the glass transitions are marked by a sharp drop in the viscoelastic moduli and a subsequent peak in the tan( $\delta$ ) which varied from 97 °C for PCPC to  $\sim 130$  °C for PvCHC and PCHC. The crossover temperature is the

point at which  $G' = G''$  and marks the end of the rubbery plateau. These are lowest for PeCHC and PCPC at 161–166 °C and increase to 192–196 °C for PCHC and stabilized PvCHC (0.1 wt% of a radical inhibitor, pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), PEHC).

To further probe the influence of polymer structure on the molecular dynamics, the samples were analyzed by variable frequency rheology, at constant 10 °C intervals, and the data was used to construct time-temperature superposition (TTS) master-curves (Figures 6a-b and S32, S34, S36 and S38, reference temperature,  $T_{ref}$ , set at 140 °C). In these investigations, the PvCHC-125 was stabilized with 0.1 wt% of PEHC to prevent cross-linking (Figure S47). The shift factors,  $a_T$ , showed excellent fits to the Williams-Landel-Ferry (WLF) equation (Table S4 and Figures S39-S4). Similar to the observations in the temperature ramps, all the polycarbonates display typical thermoplastic behavior: their viscoelastic response change from the glassy state at high frequencies to viscous flow at low frequencies, passing through a rubbery plateau at intermediate frequencies. There are, however, some notable differences in the viscoelastic parameters within the series of materials, signaling the significant influence of the polymer backbone structure on both the slow (long-distance chain entanglements) and fast (short-distance segmental rearrangements) relaxation processes. At high frequencies, the viscoelastic response should reflect short-range relaxations, i.e. molecular motions corresponding to the monomer repeat unit. In the transition zone, both of the dynamic moduli ( $G'$  and  $G''$ ) show a strong frequency dependence. This results in a characteristic maximum in the  $\tan(\delta)$  data which correlates approximately with the middle of the transition zone. The values for  $\tan(\delta)_{max}$  occur at the lowest frequencies for PCHC (4.3 Hz), which is one order of magnitude lower than for PeCHC and PvCHC (33–70 Hz), and 4 orders of magnitude lower than for PCPC (42000 Hz). The longer times needed for PCHC suggests that its cyclohexyl groups exert a greater resistance to molecular motions than alkyl-substituted rings and those with one fewer carbon atom. The resistance may arise from conformational effects, for example the cyclohexene chair conformations may move more slowly through the polymer matrix than other repeat units.<sup>46</sup>

At intermediate relaxation times, the decrease of storage and loss moduli with frequency is less severe giving rise to a plateau region in  $G'$ . In this region, the polymer viscoelastic properties are influenced by chain entanglements that restrain long-range motions. The rubbery plateau modulus,  $G_N^0$ , can be determined from the minimum of the  $\tan(\delta)$  in this region, allowing for the estimation of the entanglement molecular weight,  $M_e$ , using the tube model equation:

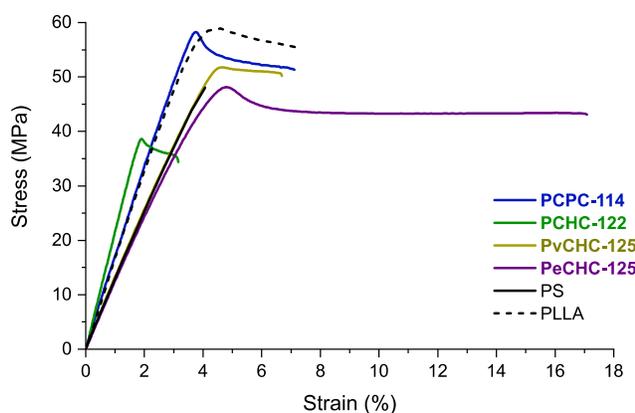
$$M_e = \frac{4}{5} \times \frac{\rho RT}{G_N^0}$$

Where  $\rho$  is the polymer density (see SI for estimates),  $R$  is the gas constant, and  $T$  is the temperature.<sup>80–81</sup>

Importantly, the best performing thermoplastics typically show low values of  $M_e$ . The comparison of this series of polymers reveals that the cyclohexyl ring polymers, PCHC and PvCHC, both show  $M_e$  values that are >10 times higher ( $\sim 56$ – $59 \text{ kg mol}^{-1}$ ) than the cyclopentyl ring substituted polymer, PCPC ( $M_e \sim 4.2 \text{ kg mol}^{-1}$ ). Due to the high molar masses and narrow dispersity values of the polymers described in this work, values of  $M_e$  obtained for PCHC are 4 times greater than those previously estimated.<sup>45–46</sup> Intriguingly, ethyl substituted PeCHC displays a somewhat intermediate value of  $M_e \sim 17 \text{ kg mol}^{-1}$  between these two extremes. It is clear from these results that ring-size and alkyl substitution directly influences the molecular dynamics, including the distance between entanglements.

Finally, at shorter frequencies and after modulus crossover, the materials begin to undergo Newtonian flow. In this region, the relaxation time,  $\tau$ , of the bulk material is correlated to the cross-over frequency where  $\tau = 1/\omega$  at the point where  $G' = G''$  (Table 2, and Table S4). In the series of polymers, PCHC shows the longest relaxation times (4 h) followed by PvCHC ( $\sim 1.5$  h), while PeCHC and PCPC had comparatively fast relaxations (0.2–1 min). In this region, the complex viscosity also reaches a plateau, i.e. the zero shear viscosity,  $\eta_0$ . At the reference temperatures, PCPC and PeCHC show 115 and 70x lower  $\eta_0$  than PCHC – another beneficial property for polymer processing.

Films of the polymers (PvCHC-125, PCHC-122, PCPC-114, and PeCHC-125) were prepared for tensile mechanical investigations by solvent casting (from methylene chloride solutions) into Teflon molds, followed by solvent evaporation, at ambient temperature for 48 h, and then by heating at 140 °C, under high vacuum, for 24 h. The resulting materials were processed by compression molding above the glass transition temperature (for 10 mins and 4 metric tonnes of pressure) to obtain homogeneous films. GPC analyses of the polymers before and after processing showed identical molar mass and dispersity values, indicating they remained stable under these conditions (Figures S52–S54). From the films, dumb-bell shaped specimens were cut, according to ISO 527-2 type 5B and subjected to unilateral extension experiments, conducted according to ISO 527 (Table 3, Figure 7 and Figure S60a). All the polycarbonates are strong plastics with variable tensile strengths, Young's moduli and toughness values. High molar mass PCPC-114 is both the strongest and most ductile, with a tensile strength reaching  $58.5 \pm 1.7 \text{ MPa}$  and strain at break of  $7.1 \pm 1.9 \%$ . The PvCHC shows a tensile strength of  $52.2 \text{ MPa}$  and strain at break  $\sim 5 \%$ . PCHC is both the weakest and most brittle, with an average tensile strength of  $40.0 \text{ MPa}$  and a strain at break of  $\sim 3 \%$ , it also has the highest Young's modulus of  $2.2 \text{ GPa}$ . The sample containing the ethyl substituent, PeCHC shows better properties than the other two six-membered ring samples, with 5x greater elongation at break ( $18.7 \pm 4.2\%$ ) and tensile toughness ( $46.7 \pm 1.3 \text{ MPa}$ ) compared with PCHC (Table 3, entry 4).



**Figure 7.** Representative stress vs. strain data for high molar mass polycarbonates, dumb-bell specimens by ISO 527, test speed of 10 mm·min<sup>-1</sup> (full data in Figures S55-58).

**Table 3. Mechanical properties of selected high molar mass polycarbonates.**

Polymer	$\sigma$ (MPa) <sup>a</sup>	$\epsilon_b$ (%) <sup>b</sup>	$E_y$ (GPa) <sup>c</sup>	$u_t$ (MJ·m <sup>-3</sup> ) <sup>d</sup>
PvCHC-125	52.2 ± 1.0	4.9 ± 1.3	1.33 ± 0.11	1.6 ± 0.6
PCHC-122	40.0 ± 1.8	3.3 ± 0.3	2.16 ± 0.06	0.9 ± 0.1
PCPC-114	58.5 ± 1.7	7.1 ± 1.9	1.70 ± 0.09	2.9 ± 1.1
PeCHC-125	46.7 ± 1.3	18.7 ± 4.2	1.31 ± 0.05	7.0 ± 1.5

<sup>a</sup>Ultimate tensile strength. <sup>b</sup>Strain at break. <sup>c</sup>Young's Modulus. <sup>d</sup>Tensile toughness. Mean values ± std. dev. from measurements conducted independently on at least 4 specimens (Figures S55-S58 for full data).

### Polycarbonate Recycling

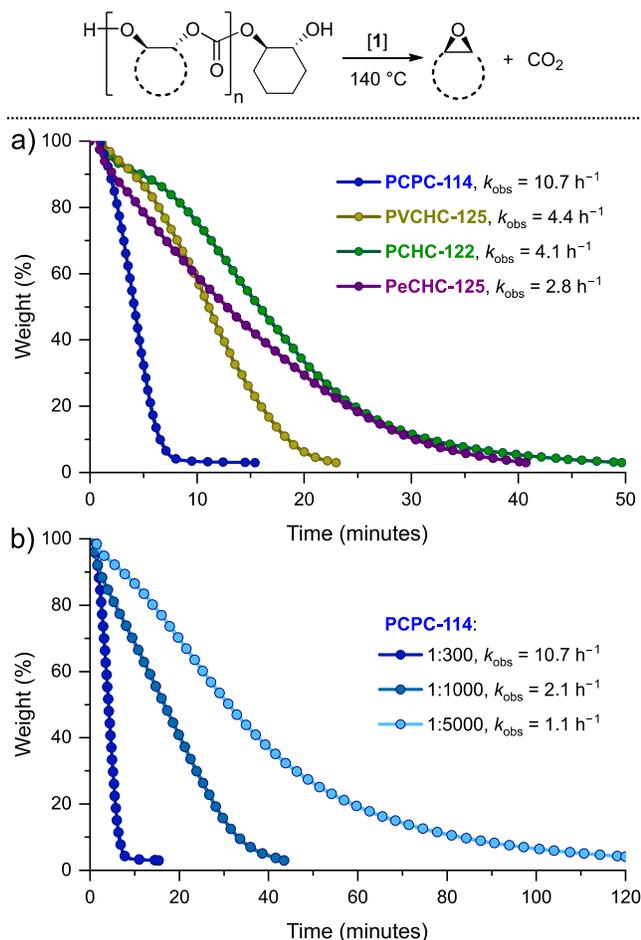
All new polymers should be investigated for efficient end-of-life recycling by both mechanical reprocessing and chemical recycling to monomers. Since these thermoplastics are all amorphous, they should be amenable to re-processing at temperatures above the  $T_g$ . The potential for mechanical recycling was explored by compression molding samples which had been subjected to mechanical testing. Samples of both PCHC-122 and PCPC-114 were re-processed into homogeneous films and their mechanical properties were tested again (Figure S60b). Both samples showed equivalent tensile mechanical profiles to the original samples, indicating the potential for future mechanical recycling of the polymers (Figure S61).

Next, the potential for polycarbonate chemical recycling to the constituent epoxides and carbon dioxide was explored in the solid state with complex **1**. Recently, we reported an efficient method for the chemical recycling of neat PCHC films, containing dispersed catalyst, and investigated depolymerization rates using polymer weight loss vs. time methods, at constant temperature, by thermogravimetric analysis.<sup>68</sup> Following the same

successful film recycling protocol, the polycarbonates were mixed with **1** in solvent (THF) and cast as films into the TGA crucibles, followed by the complete removal of the solvent (SI for details). The polymer films were chemically recycled by heating to 140 °C, at a N<sub>2</sub> flow rate of 25 mL min<sup>-1</sup>, and with continual monitoring of sample weight loss vs. time. Using catalyst **1**, at loadings of 1:300, all the polymers were efficiently depolymerized and formed only the starting *cis*-epoxide and CO<sub>2</sub> as determined by *in situ* FTIR measurements (Figure 8a, Table S6, Figures S63-66). It is noteworthy that even though the polymers are atactic, in all cases depolymerization conversion and selectivity into *cis*-epoxide is high; absolute stereochemistry does not affect depolymerization, only relative *trans*-stereochemistry is important for chain-end backbiting to occur (Figure S67).

In all cases, the recycling occurred quickly, with typical turn-over-frequency (TOF) values of 700-1400 h<sup>-1</sup>. The chemical recycling rates were fastest for the PCPC and decreased in the order PCPC > PvCHC > PeCHC ~ PCHC. The rate differences are proposed to arise from different stabilities for the alkoxide intermediates and/or from different transition state barriers to epoxide extrusion.<sup>63</sup> Given the fast rates and promising thermal/mechanical properties of PCPC, it was selected for further insights into depolymerization catalysis. As such, progressively lower loadings of catalyst were explored for the depolymerization reactions (Figure 8b). All depolymerizations were successful, yielding only epoxide (CPO) and CO<sub>2</sub>, and could be achieved at catalyst loadings of just 0.02 mol% (1:5000) and with a high TOF value of 2500 h<sup>-1</sup> (Table S6). Finally, a larger-scale chemical recycling was conducted using ~2 g of PCPC ([**1**]:[PCPC] 1:1000) in glassware (see SI). After 1 h, at 140 °C, the epoxide was isolated in 72% yield and high purity as indicated by <sup>1</sup>H NMR spectroscopy (Figures S68). The depolymerization mechanism was studied for catalyst **2** in our prior work, where we proposed that depolymerization occurs *via* a chain-end mechanism. It is postulated that catalyst **1** operates by the same mechanism: when acetyl-end capped PCHC (PCHC-OAc, Figure S69 for end-group analyses) was subjected to depolymerization conditions, no reaction occurred (Figure S70). Hydrolysis of the organometallic catalyst to form the alkoxide intermediate does not occur, a key step in chain-end depolymerization, hence why no reaction is observed.

It is worth noting that a thermally crosslinked sample of PvCHC also underwent chemical depolymerization to vCHO under isothermal depolymerization at 140 °C in the TGA furnace (see SI and Figures S71-S72) and in the bulk. The non-volatility under these conditions of the putative bis-epoxide crosslinker is expected since it was not detected by <sup>1</sup>H NMR in the isolated monomer fraction (Figure S73). The 94% weight loss indicated a lightly crosslinked sample, i.e., only containing 6% weight of thermosetting units which, notably, did not impede its efficient depolymerization.



**Figure 8.** Isothermal TGA data at 140 °C comparing the chemical recycling of the polycarbonates in the presence of complex **1**: (a) constant [1]:[polycarbonate] (repeat unit) ratio of 1:300; (b) PCPC depolymerization with variable [1]:[PCPC] (repeat unit) ratio (SI for details). The data were fit using exponential functions which allow for determination of recycling rates.

## Discussion

This work has established a successful new organometallic catalyst to produce a series of CO<sub>2</sub>-based polycarbonates, evaluated their properties, and recommended upon conditions for future re-processing and depolymerization as a means of manufacture. Moreover, the catalysis advances described herein yield polycarbonates with sufficiently high molar mass values to more accurately determine and compare  $M_e$  values. The data are also fully consistent with the difficulties in processing and testing brittle PCHC: almost all most prior investigations used samples which were below the critical molar mass or chain entanglement thresholds.<sup>43, 45-46, 54, 56</sup> Certainly, the steep frequency dependence of the  $G'$  data in the rubbery plateau region makes the evaluation of  $M_e$  still somewhat challenging, and more refined estimates from the value of  $\sim 56 \text{ kg mol}^{-1}$  might still be possible in future. In contrast, the much less widely investigated PCPC, shows an order of magnitude lower  $M_e$ , with entanglement being of the same magnitude as other strong thermoplastics, e.g. BPA-PC  $M_e = 1.6\text{--}4.8 \text{ kg mol}^{-1}$ , and is considerably lower

than brittle thermoplastics, e.g. PLLA,  $M_e = 8\text{--}10 \text{ kg mol}^{-1}$ ,<sup>82</sup> PS =  $13\text{--}18 \text{ kg mol}^{-1}$ .<sup>83</sup> These data all suggest that future applications requiring high tensile strength and toughness should prioritize the five membered cyclopentene or the ethyl substituted cyclohexene ring substituents since the optimal thermal-mechanical properties will be accessed at substantially lower molar masses than the six-membered ring analogue.

Our mechanical data on the series of polycarbonates show that the most promising samples, PCPC and PeCHC, show promising properties with some in the range of existing commercial thermoplastics (Table S5). For example, PCPC has similar tensile mechanical properties to PLLA but is fully amorphous and shows a significantly higher glass transition temperature than PLLA which would extend its upper use temperature (PCPC  $T_g = 85 \text{ °C}$  vs. PLLA  $T_g = 50\text{--}60 \text{ °C}$ , respectively). Further, PCPC can undergo lower energy mechanical recycling than PLLA, since the melting temperature for PLLA is typically  $160\text{--}180 \text{ °C}$  whereas PCPC was effectively mechanically recycled, by compression molding, at  $100 \text{ °C}$  and displays a  $\eta_0$  of  $0.78 \text{ MPa s}$ .<sup>84</sup> It is important to emphasize that, as an added benefit, the high carbonate linkage content in PCPC delivers 34 wt% carbon dioxide utilization (vs. 30 wt% for PCHC). To maximize carbon dioxide utilization, the epoxide could also be sourced from biomass – there are already efficient routes to cyclopentene from lignocellulosic biomass since it is proposed for use in bio-based aviation fuels.<sup>85</sup> The synthesis involves bio-derived furfuraldehyde being hydrogenated, over copper catalysts, to cyclopentanol in 60-90% yield and subsequent alcohol dehydration to cyclopentene, achieved in 84% yield using a recyclable solid acid catalyst.<sup>85-86</sup>

Our investigation also rationalizes the lack of development of PCHC as a stand-alone material – very few catalysts have ever accessed the optimal molar masses for properties and in any case the high zero shear viscosity ( $90 \text{ MPa s}$ ) and moderate tensile mechanical properties suggest it would be best applied within copolymer structures in future.<sup>38, 47-48, 54</sup> In contrast, PeCHC, featuring an ethyl substituent on the cyclohexene ring, combines high tensile strength ( $47 \text{ MPa}$ ), reasonable ductility (19% elongation at break), high glass transition temperatures ( $105 \text{ °C}$ ), low entanglement molar mass ( $15\text{--}19 \text{ kg mol}^{-1}$ ) and low zero shear viscosity ( $1.26 \text{ MPa.s}$ ). It is recommended for further development as a thermoplastic and may inspire investigation of other substituted cyclohexane rings. Given that using bio-derived epoxides may also help increase carbon dioxide uptake, terpenes such as limonene or methene also feature substituted cyclohexane rings and their epoxides have precedent in this catalysis.<sup>67, 87-91</sup> Limonene oxide is challenging to polymerize due to its tertiary structure,<sup>89-90</sup> but menth-2-ene oxide is an important future target given the influence in this work of ethyl substituents.<sup>92</sup> Greiner and Agarwal reported a route to prepare moderate molar mass poly(meth-2-ene carbonate) ( $M_n = 20\text{--}30 \text{ kg mol}^{-1}$ ) and the polymer showed a higher glass transition temperature ( $T_g = 144 \text{ °C}$ ) and higher temperature stability ( $T_d = 308 \text{ °C}$ ) than PCHC.<sup>92</sup> In

future, the organometallic Mg(II)Co(II) catalyst could be used to target molar mass of poly(menth-2-ene carbonate) and determine its entanglement molar mass, tensile mechanical properties and zero shear viscosity.

In the chemical recycling of polycarbonates to epoxides and carbon dioxide, complex **1** combines high rates, outstanding selectivity, low loading tolerance and operates effectively using high molar mass polycarbonate – it is fastest using PCPC. Compared with other efficient PCPC depolymerization catalysts and processes its performance is excellent (Table S6). For example, catalyst **1** compares favorably against one of the best catalysts yet reported for PCPC recycling (Figure S62 for catalyst structures).<sup>48</sup> The ammonium diborane catalyst is highly effective but requires addition of KOH for activity. Even so, complex **1** enables depolymerization at 100x lower loading and shows ~2000x higher activity. **1** is also more active than [Cr(salen)(Cl)]/PPN(N<sub>3</sub>) catalyst system which operates in neat polymer, showing efficient depolymerization at 60 °C lower temperature, using 10x lower loading and at ~4x higher activity.<sup>65</sup> Complex **1** also surpasses the original [Cr(salen)(Cl)]/<sup>n</sup>Bu<sub>4</sub>NN<sub>3</sub> catalyst, used in solution in Darensbourg and co-workers' seminal work, achieving activity values that are ~ 2500x higher and operating at 1/100 loading.<sup>61</sup> These data also support future focus on PCPC since it shows the most efficient chemical recycling catalysis and allowed, in laboratory scale experiments, for efficient closed loop recycling to cyclopentene oxide and CO<sub>2</sub>.

## Conclusions

A new organometallic Mg(II)Co(II) catalyst, applied with a diol, showed outstanding productivity and initiation control in the ROCOP of CO<sub>2</sub> and cyclic epoxides. It was used to make a series of high molar mass polycarbonates, with *M<sub>n</sub>* from 100–163 kg mol<sup>-1</sup>, by copolymerization of CO<sub>2</sub> with vCHO, CHO or CPO. The physical properties of these carbon dioxide-thermoplastics, together with an ethyl-substituted eCHO derived by hydrogenation of vinyl-polycarbonate, were investigated. The thermal, mechanical and rheological experiments all demonstrate the significant influence of the ring size and alkyl-substituents over properties. The most widely investigated material in the literature, PCHC, showed a high temperature glass transition but suffered with low tensile strength and brittleness due to a lack of chain entanglements. Its entanglement molar mass, *M<sub>e</sub>*, was very high (56 kg mol<sup>-1</sup>) which complicates future processing and applications. Achieving optimal properties will require ultra-high molar mass samples (> 10<sup>3</sup> kg mol<sup>-1</sup>),<sup>93-96</sup> with concomitant processing limitations due to its high viscosity. As such, perhaps it will be better to limit use of PCHC as a stand-alone material and investigate its beneficial properties within copolymer structures. On the other hand, exactly the opposite conclusion is made regarding PCPC which shows significant potential as a future thermoplastic. A PCPC with molar mass 114 kg mol<sup>-1</sup> showed high tensile strength (59 MPa), high Young's modulus (1.7 GPa), moderate elongation at break (7%),

high tensile toughness (3 MJm<sup>-3</sup>), a medium/high glass transition temperature (*T<sub>g</sub>* = 85 or 97 °C by DSC or rheology) and low zero shear viscosity (0.78 MPa.s). These properties arise from its low *M<sub>e</sub>* (4-5 kg mol<sup>-1</sup>) with the consequence that in future only moderate molar mass polymers should be required to achieve the best material properties. Its properties are similar to those of polystyrene, albeit with a lower *M<sub>e</sub>*, and it improves upon the high use temperature limitations of poly(L-lactide) (PLLA). All the polycarbonates, including PCPC, are fully re-processable by compression molding (100-140 °C, 10 mins) providing a future mechanical recycling route. Further, the new Mg(II)Co(II) catalyst efficiently depolymerized the high molar mass polycarbonates to epoxides and CO<sub>2</sub>, providing a future chemical recycling option. The lead material, PCPC, underwent the fastest depolymerizations with high activity (TOF = 2500 h<sup>-1</sup>) and low catalyst loadings (1:5000), exceeding performances by several orders for current literature catalysts. In future, PCPC should be prioritized for further investigation both in catalysis, application development and recycling chemistry. The new organometallic Mg(II)Co(II) catalyst, with its high productivity, low loading and efficiency in either CO<sub>2</sub> polymerization or depolymerization, should be investigated using other monomers and polymerizations to diversify the range of CO<sub>2</sub>-based polymers.

## ASSOCIATED CONTENT

### Supporting information

The Supporting Information is available free of charge at <http://pubs.acs.org>

Characterization data of complexes (NMR, X-ray crystallography, magnetic moment, cyclic voltammetry); polymerization data (NMR, MALDI-ToF, GPC chromatograms, DSC, TGA, Rheology, Tensile Testing); chemical recycling data (NMR, TGA-FTIR) (insert PDF link);

CheckCIF/PLATON report (insert PDF link)

### Accession Codes

CCDC 2208898-2208899 contains the supplementary crystallographic data for this paper. These data can be obtained via [www.ccdc-cam.ac.uk/data](http://www.ccdc-cam.ac.uk/data)

## AUTHOR INFORMATION

### Notes

The authors declare the following competing financial interest(s): C. K. W. is a director of Eonic Technologies Ltd.

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## References

- (1) Bachmann, M.; Zibunas, C.; Hartmann, J.; Tulus, V.; Suh, S.; Guillén-Gosálbez, G.; Bardow, A., Towards circular plastics within planetary boundaries. *Nat. Sustain.* **2023**, *6* (5), 599-610. 10.1038/s41893-022-01054-9.
- (2) Zheng, J.; Suh, S., Strategies to reduce the global carbon footprint of plastics. *Nat. Clim. Change.* **2019**, *9* (5), 374-378. 10.1038/s41558-019-0459-z.
- (3) Nicholson, S. R.; Rorrer, N. A.; Carpenter, A. C.; Beckham, G. T., Manufacturing energy and greenhouse gas emissions associated with plastics consumption. *Joule* **2021**, *5* (3), 673-686. <https://doi.org/10.1016/j.joule.2020.12.027>.
- (4) Jehanno, C.; Alty, J. W.; Roosen, M.; De Meester, S.; Dove, A. P.; Chen, E. Y. X.; Leibfarth, F. A.; Sardon, H., Critical advances and future opportunities in upcycling commodity polymers. *Nature* **2022**, *603* (7903), 803-814. 10.1038/s41586-021-04350-0.
- (5) Haque, F. M.; Ishibashi, J. S. A.; Lidston, C. A. L.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; Ellison, C. J.; Gormong, E. A.; Hamachi, L. S.; Hoye, T. R.; Jin, M.; Kalow, J. A.; Kim, H. J.; Kumar, G.; LaSalle, C. J.; Liffland, S.; Lipinski, B. M.; Pang, Y.; Parveen, R.; Peng, X.; Popowski, Y.; Prebhalo, E. A.; Reddi, Y.; Reineke, T. M.; Sheppard, D. T.; Swartz, J. L.; Tolman, W. B.; Vlaisavljevich, B.; Wissinger, J.; Xu, S.; Hillmyer, M. A., Defining the Macromolecules of Tomorrow through Synergistic Sustainable Polymer Research. *Chem. Rev.* **2022**, *122* (6), 6322-6373. 10.1021/acs.chemrev.1c00173.
- (6) Stegmann, P.; Daioglou, V.; Londo, M.; van Vuuren, D. P.; Junginger, M., Plastic futures and their CO<sub>2</sub> emissions. *Nature* **2022**, *612* (7939), 272-276. 10.1038/s41586-022-05422-5.
- (7) Coates, G. W.; Getzler, Y. D. Y. L., Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* **2020**, *5* (7), 501-516. 10.1038/s41578-020-0190-4.
- (8) Hong, M.; Chen, E. Y. X., Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of  $\gamma$ -butyrolactone. *Nat. Chem.* **2016**, *8* (1), 42-49. 10.1038/nchem.2391.
- (9) Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M., Catalysis as an Enabling Science for Sustainable Polymers. *Chem. Rev.* **2018**, *118* (2), 839-885. 10.1021/acs.chemrev.7b00329.
- (10) Schneiderman, D. K.; Hillmyer, M. A., 50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers. *Macromolecules* **2017**, *50* (10), 3733-3749. 10.1021/acs.macromol.7b00293.
- (11) Hepburn, C.; Adlen, E.; Beddington, J.; Carter, E. A.; Fuss, S.; Mac Dowell, N.; Minx, J. C.; Smith, P.; Williams, C. K., The technological and economic prospects for CO<sub>2</sub> utilization and removal. *Nature* **2019**, *575* (7781), 87-97. 10.1038/s41586-019-1681-6.
- (12) Bhat, G. A.; Darensbourg, D. J., Progress in the catalytic reactions of CO<sub>2</sub> and epoxides to selectively provide cyclic or polymeric carbonates. *Green Chem.* **2022**, *24* (13), 5007-5034. 10.1039/D2GC01422J.
- (13) Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C., Advances in the use of CO<sub>2</sub> as a renewable feedstock for the synthesis of polymers. *Chem. Soc. Rev.* **2019**, *48* (16), 4466-4514. 10.1039/C9C500047J.
- (14) Lee, S. H.; Cyriac, A.; Jeon, J. Y.; Lee, B. Y., Preparation of thermoplastic polyurethanes using in situ generated poly(propylene carbonate)-diols. *Polym. Chem.* **2012**, *3* (5), 1215-1220. 10.1039/C2PY00010E.
- (15) Schüttner, S.; Gardiner, C.; Petrov, F. S.; Fotaras, N.; Preis, J.; Floudas, G.; Frey, H., Biobased Thermoplastic Elastomers Derived from Citronellyl Glycidyl Ether, CO<sub>2</sub>, and Polylactide. *Macromolecules* **2023**, *56* (20), 8247-8259. 10.1021/acs.macromol.3c01329.
- (16) Scharfenberg, M.; Hofmann, S.; Preis, J.; Hilf, J.; Frey, H., Rigid Hyperbranched Polycarbonate Polyols from CO<sub>2</sub> and Cyclohexene-Based Epoxides. *Macromolecules* **2017**, *50* (16), 6088-6097. 10.1021/acs.macromol.7b01276.
- (17) Scharfenberg, M.; Hilf, J.; Frey, H., Functional Polycarbonates from Carbon Dioxide and Tailored Epoxide Monomers: Degradable Materials and Their Application Potential. *Adv. Funct. Mater.* **2018**, *28* (10), 1704302. <https://doi.org/10.1002/adfm.201704302>.
- (18) Yang, G.-W.; Wu, G.-P., High-Efficiency Construction of CO<sub>2</sub>-Based Healable Thermoplastic Elastomers via a Tandem Synthetic Strategy. *ACS Sustain. Chem. Eng.* **2019**, *7* (1), 1372-1380. 10.1021/acssuschemeng.8b05084.
- (19) Cao, H.; Zhang, R.; Zhou, Z.; Liu, S.; Tao, Y.; Wang, F.; Wang, X., On-Demand Transformation of Carbon Dioxide into Polymers Enabled by a Comb-Shaped Metallic Oligomer Catalyst. *ACS Catal.* **2022**, *12* (1), 481-490. 10.1021/acscatal.1c04431.
- (20) Deng, J.; Ratanasak, M.; Sako, Y.; Tokuda, H.; Maeda, C.; Hasegawa, J.-y.; Nozaki, K.; Ema, T., Aluminum porphyrins with quaternary ammonium halides as catalysts for copolymerization of cyclohexene oxide and CO<sub>2</sub>: metal-ligand cooperative catalysis. *Chem. Sci.* **2020**, *11* (22), 5669-5675. 10.1039/D0SC01609H.
- (21) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K., Highly Active Dizinc Catalyst for the Copolymerization of Carbon Dioxide and Cyclohexene Oxide at One Atmosphere Pressure. *Angew. Chem. Int. Ed.* **2009**, *48* (5), 931-933. <https://doi.org/10.1002/anie.200803896>.
- (22) Rosetto, G.; Deacy, A. C.; Williams, C. K., Mg(ii) heterodinuclear catalysts delivering carbon dioxide derived multi-block polymers. *Chem. Sci.* **2021**, *12* (37), 12315-12325. 10.1039/D1SC03856G.
- (23) Nagae, H.; Aoki, R.; Akutagawa, S.-n.; Kleemann, J.; Tagawa, R.; Schindler, T.; Choi, G.; Spaniol, T. P.; Tsurugi, H.; Okuda, J.; Mashima, K., Lanthanide Complexes Supported by a Trizinc Crown Ether as Catalysts for Alternating Copolymerization of Epoxide and CO<sub>2</sub>: Telomerization Controlled by Carboxylate Anions. *Angew. Chem. Int. Ed.* **2018**, *57* (9), 2492-2496. <https://doi.org/10.1002/anie.201709218>.
- (24) Deacy, A. C.; Phanopoulos, A.; Lindeboom, W.; Buchard, A.; Williams, C. K., Insights into the Mechanism of Carbon Dioxide and Propylene Oxide Ring-Opening Copolymerization Using a Co(III)/K(I) Heterodinuclear Catalyst. *J. Am. Chem. Soc.* **2022**, *144* (39), 17929-17938. 10.1021/jacs.2c06921.
- (25) Lindeboom, W.; Deacy, A. C.; Phanopoulos, A.; Buchard, A.; Williams, C. K., Correlating Metal Redox Potentials to Co(III)/K(I) Catalyst Performances in Carbon Dioxide and Propene Oxide Ring Opening Copolymerization. *Angew. Chem. Int. Ed.* **2023**, *62* (37), e202308378. <https://doi.org/10.1002/anie.202308378>.
- (26) Diment, W. T.; Lindeboom, W.; Fiorentini, F.; Deacy, A. C.; Williams, C. K., Synergic Heterodinuclear Catalysts for the Ring-Opening Copolymerization (ROCOP) of Epoxides, Carbon Dioxide, and Anhydrides. *Acc. Chem. Res.* **2022**, *55* (15), 1997-2010. 10.1021/acs.accounts.2c00197.
- (27) Deacy, A. C.; Kilpatrick, A. F. R.; Regoutz, A.; Williams, C. K., Understanding metal synergy in heterodinuclear catalysts for the copolymerization of CO<sub>2</sub> and epoxides. *Nat. Chem.* **2020**, *12* (4), 372-380. 10.1038/s41557-020-0450-3.
- (28) Cheng, M.; Lobkovsky, E. B.; Coates, G. W., Catalytic Reactions Involving C<sub>1</sub> Feedstocks: New High-Activity Zn(II)-Based Catalysts for the Alternating Copolymerization of Carbon Dioxide and Epoxides. *J. Am. Chem. Soc.* **1998**, *120* (42), 11018-11019. 10.1021/ja982601k.
- (29) Lehenmeier, M. W.; Kissling, S.; Altenbuchner, P. T.; Bruckmeier, C.; Deglmann, P.; Brym, A.-K.; Rieger, B., Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO<sub>2</sub>/Epoxide Copolymerization Catalysis? *Angew. Chem. Int. Ed.* **2013**, *52* (37), 9821-9826. <https://doi.org/10.1002/anie.201302157>.
- (30) Liu, Y.; Ren, W.-M.; Liu, J.; Lu, X.-B., Asymmetric Copolymerization of CO<sub>2</sub> with meso-Epoxides Mediated by Dinuclear

- Cobalt(III) Complexes: Unprecedented Enantioselectivity and Activity. *Angew. Chem. Int. Ed.* **2013**, *52* (44), 11594-11598. <https://doi.org/10.1002/anie.201305154>.
- (31) Asaba, H.; Iwasaki, T.; Hatazawa, M.; Deng, J.; Nagae, H.; Mashima, K.; Nozaki, K., Alternating Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide Catalyzed by Cobalt-Lanthanide Mixed Multinuclear Complexes. *Inorg. Chem.* **2020**, *59* (12), 7928-7933. 10.1021/acs.inorgchem.0c01156.
- (32) Yang, G.-W.; Zhang, Y.-Y.; Xie, R.; Wu, G.-P., Scalable Bifunctional Organoboron Catalysts for Copolymerization of CO<sub>2</sub> and Epoxides with Unprecedented Efficiency. *J. Am. Chem. Soc.* **2020**, *142* (28), 12245-12255. 10.1021/jacs.0c03651.
- (33) Taherimehr, M.; Al-Amsyar, S. M.; Whiteoak, C. J.; Kleij, A. W.; Pescarmona, P. P., High activity and switchable selectivity in the synthesis of cyclic and polymeric cyclohexene carbonates with iron amino triphenolate catalysts. *Green Chem.* **2013**, *15* (11), 3083-3090. 10.1039/C3GC41303A.
- (34) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L., (Salen)Cr(III) Catalysts for the Copolymerization of Carbon Dioxide and Epoxides: Role of the Initiator and Cocatalyst. *Inorg. Chem.* **2004**, *43* (6), 1831-1833. 10.1021/ic0352856.
- (35) Schütze, M.; Dechert, S.; Meyer, F., Highly Active and Readily Accessible Proline-Based Zinc Catalyst for CO<sub>2</sub>/Epoxide Copolymerization. *Chem. - Eur. J.* **2017**, *23* (65), 16472-16475. <https://doi.org/10.1002/chem.201704754>.
- (36) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W., Bimetallic Anilido-Aldimine Zinc Complexes for Epoxide/CO<sub>2</sub> Copolymerization. *J. Am. Chem. Soc.* **2005**, *127* (9), 3031-3037. 10.1021/ja0435135.
- (37) Zhang, D.; Boopathi, S. K.; Hadjichristidis, N.; Gnanou, Y.; Feng, X., Metal-Free Alternating Copolymerization of CO<sub>2</sub> with Epoxides: Fulfilling "Green" Synthesis and Activity. *J. Am. Chem. Soc.* **2016**, *138* (35), 1117-1120. 10.1021/jacs.6b06679.
- (38) Zhang, J.; Wang, L.; Liu, S.; Li, Z., Synthesis of Diverse Polycarbonates by Organocatalytic Copolymerization of CO<sub>2</sub> and Epoxides: From High Pressure and Temperature to Ambient Conditions. *Angew. Chem. Int. Ed.* **2022**, *61* (4), e20211197. <https://doi.org/10.1002/anie.20211197>.
- (39) Kozak, C. M.; Ambrose, K.; Anderson, T. S., Copolymerization of carbon dioxide and epoxides by metal coordination complexes. *Coord. Chem. Rev.* **2018**, *376*, 565-587. <https://doi.org/10.1016/j.ccr.2018.08.019>.
- (40) Chen, C.; Gnanou, Y.; Feng, X., Ultra-Productive Upcycling CO<sub>2</sub> into Polycarbonate Polyols via Borinane-Based Bifunctional Organocatalysts. *Macromolecules* **2023**, *56* (3), 892-898. 10.1021/acs.macromol.2c02243.
- (41) Schaefer, J.; Zhou, H.; Lee, E.; Lambic, N. S.; Culcu, G.; Holtcamp, M. W.; Rix, F. C.; Lin, T.-P., Tertiary and Quaternary Phosphonium Borane Bifunctional Catalysts for CO<sub>2</sub>/Epoxide Copolymerization: A Mechanistic Investigation Using In Situ Raman Spectroscopy. *ACS Catal.* **2022**, *12* (19), 11870-11885. 10.1021/acscatal.2c03843.
- (42) Darensbourg, D. J., Chain transfer agents utilized in epoxide and CO<sub>2</sub> copolymerization processes. *Green Chem.* **2019**, *21* (9), 2214-2223. 10.1039/C9GC00620F.
- (43) Sulley, G. S.; Gregory, G. L.; Chen, T. T. D.; Peña Carrodegua, L.; Trott, G.; Santmarti, A.; Lee, K.-Y.; Terrill, N. J.; Williams, C. K., Switchable Catalysis Improves the Properties of CO<sub>2</sub>-Derived Polymers: Poly(cyclohexene carbonate-*b*-ε-decalactone-*b*-cyclohexene carbonate) Adhesives, Elastomers, and Toughened Plastics. *J. Am. Chem. Soc.* **2020**, *142* (9), 4367-4378. 10.1021/jacs.9b13106.
- (44) Jutz, F.; Buchard, A.; Kember, M. R.; Fredriksen, S. B.; Williams, C. K., Mechanistic Investigation and Reaction Kinetics of the Low-Pressure Copolymerization of Cyclohexene Oxide and Carbon Dioxide Catalyzed by a Zinc Complex. *J. Am. Chem. Soc.* **2011**, *133* (43), 17395-17405. 10.1021/ja206352x.
- (45) Koning, C.; Wildeson, J.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J., Synthesis and physical characterization of poly(cyclohexane carbonate), synthesized from CO<sub>2</sub> and cyclohexene oxide. *Polymer* **2001**, *42* (9), 3995-4004. [https://doi.org/10.1016/S0032-3861\(00\)00709-6](https://doi.org/10.1016/S0032-3861(00)00709-6).
- (46) Spyridakou, M.; Gardiner, C.; Papamokos, G.; Frey, H.; Floudas, G., Dynamics of Poly(cyclohexene carbonate) as a Function of Molar Mass. *ACS Appl. Polym. Mater.* **2022**, *4* (5), 3833-3843. 10.1021/acscpm.2c00299.
- (47) Jia, M.; Hadjichristidis, N.; Gnanou, Y.; Feng, X., Monomodal Ultrahigh-Molar-Mass Polycarbonate Homopolymers and Diblock Copolymers by Anionic Copolymerization of Epoxides with CO<sub>2</sub>. *ACS Macro Lett.* **2019**, *8* (12), 1594-1598. 10.1021/acsmacrolett.9b00854.
- (48) Yang, G.-W.; Wang, Y.; Qi, H.; Zhang, Y.-Y.; Zhu, X.-F.; Lu, C.; Yang, L.; Wu, G.-P., Highly Selective Preparation and Depolymerization of Chemically Recyclable Poly(cyclopentene carbonate) Enabled by Organoboron Catalysts. *Angew. Chem. Int. Ed.* **2022**, *61* (46), e202210243. <https://doi.org/10.1002/anie.202210243>.
- (49) Ren, W.-M.; Zhang, X.; Liu, Y.; Li, J.-F.; Wang, H.; Lu, X.-B., Highly Active, Bifunctional Co(III)-Salen Catalyst for Alternating Copolymerization of CO<sub>2</sub> with Cyclohexene Oxide and Terpolymerization with Aliphatic Epoxides. *Macromolecules* **2010**, *43* (3), 1396-1402. 10.1021/ma902321g.
- (50) Kong, D.-C.; Yang, M.-H.; Zhang, X.-S.; Du, Z.-C.; Fu, Q.; Gao, X.-Q.; Gong, J.-W., Control of Polymer Properties by Entanglement: A Review. *Macromol. Mater. Eng.* **2021**, *306* (12), 2100536. <https://doi.org/10.1002/mame.202100536>.
- (51) Jia, M.; Zhang, D.; de Kort, G. W.; Wilsens, C. H. R. M.; Rastogi, S.; Hadjichristidis, N.; Gnanou, Y.; Feng, X., All-Polycarbonate Thermoplastic Elastomers Based on Triblock Copolymers Derived from Triethylborane-Mediated Sequential Copolymerization of CO<sub>2</sub> with Various Epoxides. *Macromolecules* **2020**, *53* (13), 5297-5307. 10.1021/acs.macromol.0c01068.
- (52) Neumann, S.; Däbritz, S. B.; Fritze, S. E.; Leitner, L.-C.; Anand, A.; Greiner, A.; Agarwal, S., Sustainable block copolymers of poly(limonene carbonate). *Polym. Chem.* **2021**, *12* (6), 903-910. 10.1039/D0PY01685C.
- (53) Liu, J.; Jia, M.; Gnanou, Y.; Feng, X., One-Pot Synthesis of CO<sub>2</sub>-Based Polylactide-*b*-Poly(ether carbonate)-*b*-Polylactide Triblock Copolymers and Their Mechanical Properties. *Macromolecules* **2023**, *56* (4), 1615-1624. 10.1021/acs.macromol.2c02522.
- (54) Kernbichl, S.; Rieger, B., Aliphatic polycarbonates derived from epoxides and CO<sub>2</sub>: A comparative study of poly(cyclohexene carbonate) and poly(limonene carbonate). *Polymer* **2020**, *205*, 122667. <https://doi.org/10.1016/j.polymer.2020.122667>.
- (55) Hauenstein, O.; Reiter, M.; Agarwal, S.; Rieger, B.; Greiner, A., 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* (3), 760-770. 10.1039/C5GC01694K.
- (56) Bailer, J.; Feth, S.; Bretschneider, F.; Rosenfeldt, S.; Drechsler, M.; Abetz, V.; Schmalz, H.; Greiner, A., Synthesis and self-assembly of biobased poly(limonene carbonate)-block-poly(cyclohexene carbonate) diblock copolymers prepared by sequential ring-opening copolymerization. *Green Chem.* **2019**, *21* (9), 2266-2272. 10.1039/C9GC00250B.
- (57) Romain, C.; Garden, J. A.; Trott, G.; Buchard, A.; White, A. J. P.; Williams, C. K., Di-Zinc-Aryl Complexes: CO<sub>2</sub> Insertions and Applications in Polymerisation Catalysis. *Chem. - Eur. J.* **2017**, *23* (30), 7367-7376. <https://doi.org/10.1002/chem.201701013>.
- (58) Diment, W. T.; Williams, C. K., Chain end-group selectivity using an organometallic Al(iii)/K(i) ring-opening copolymerization catalyst delivers high molar mass, monodisperse polyesters. *Chem. Sci.* **2022**, *13* (29), 8543-8549. 10.1039/D2SC02752F.
- (59) Liu, Y.; Lu, X.-B., Emerging Trends in Closed-Loop Recycling Polymers: Monomer Design and Catalytic Bulk Depolymerization. *Chem. - Eur. J.* **2023**, *29* (23), e202203635. <https://doi.org/10.1002/chem.202203635>.
- (60) Liu, Y.; Lu, X.-B., Chemical recycling to monomers: Industrial Bisphenol-A-Polycarbonates to novel aliphatic polycarbonate materials. *J. Polym. Sci.* **2022**, *60* (24), 3256-3268. <https://doi.org/10.1002/pol.2022018>.
- (61) Darensbourg, D. J.; Wei, S.-H.; Yeung, A. D.; Ellis, W. C., An Efficient Method of Depolymerization of Poly(cyclopentene carbonate) to Its Comonomers: Cyclopentene Oxide and Carbon Dioxide. *Macromolecules* **2013**, *46* (15), 5850-5855. 10.1021/ma401286x.

- (62) Liu, Y.; Zhou, H.; Guo, J.-Z.; Ren, W.-M.; Lu, X.-B., Completely Recyclable Monomers and Polycarbonate: Approach to Sustainable Polymers. *Angew. Chem. Int. Ed.* **2017**, *56* (17), 4862-4866. <https://doi.org/10.1002/anie.201701438>.
- (63) Singer, F. N.; Deacy, A. C.; McGuire, T. M.; Williams, C. K.; Buchard, A., Chemical Recycling of Poly(Cyclohexene Carbonate) Using a Di-MgII Catalyst. *Angew. Chem. Int. Ed.* **2022**, *61* (26), e202201785. <https://doi.org/10.1002/anie.202201785>.
- (64) Liao, X.; Cui, F.-C.; He, J.-H.; Ren, W.-M.; Lu, X.-B.; Zhang, Y.-T., A sustainable approach for the synthesis of recyclable cyclic CO<sub>2</sub>-based polycarbonates. *Chem. Sci.* **2022**, *13* (21), 6283-6290. [10.1039/D2SC01387H](https://doi.org/10.1039/D2SC01387H).
- (65) Yu, Y.; Gao, B.; Liu, Y.; Lu, X.-B., Efficient and Selective Chemical Recycling of CO<sub>2</sub>-Based Alicyclic Polycarbonates via Catalytic Pyrolysis. *Angew. Chem. Int. Ed.* **2022**, *61* (34), e202204492. <https://doi.org/10.1002/anie.202204492>.
- (66) Yu, Y.; Fang, L.-M.; Liu, Y.; Lu, X.-B., Chemical Synthesis of CO<sub>2</sub>-Based Polymers with Enhanced Thermal Stability and Unexpected Recyclability from Biosourced Monomers. *ACS Catal.* **2021**, *11* (13), 8349-8357. [10.1021/acscatal.1c01376](https://doi.org/10.1021/acscatal.1c01376).
- (67) Carrodegua, L. P.; Chen, T. D.; Gregory, G. L.; Sulley, G. S.; Williams, C. K., High elasticity, chemically recyclable, thermoplastics from bio-based monomers: carbon dioxide, limonene oxide and ε-decalactone. *Green Chem.* **2020**, *22* (23), 8298-8307. [10.1039/D0GC02295K](https://doi.org/10.1039/D0GC02295K).
- (68) McGuire, T. M.; Deacy, A. C.; Buchard, A.; Williams, C. K., 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* (40), 18444-18449. [10.1021/jacs.2c06937](https://doi.org/10.1021/jacs.2c06937).
- (69) Royo, P.; Vazquez, A., Pentafluorophenylcobalt(II) complexes. *J. Organomet. Chem.* **1981**, *204* (2), 243-247. [https://doi.org/10.1016/S0022-328X\(00\)84590-8](https://doi.org/10.1016/S0022-328X(00)84590-8).
- (70) Smith, C. F.; Tamborski, C., Synthesis and reactions of a bis(pentafluorophenyl)cobalt complex. *J. Organomet. Chem.* **1971**, *32* (2), 257-262. [https://doi.org/10.1016/S0022-328X\(00\)85078-0](https://doi.org/10.1016/S0022-328X(00)85078-0).
- (71) Rossi, A. R.; Hoffmann, R., Transition metal pentacoordination. *Inorg. Chem.* **1975**, *14* (2), 365-374. [10.1021/ic50144a032](https://doi.org/10.1021/ic50144a032).
- (72) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W., Enantiomerically-enriched organic reagents polymer synthesis: enantioselective copolymerization of cycloalkene oxides and CO using homogeneous, zinc-based catalysts. *Chem. Commun.* **2000**, (20), 2007-2008. [10.1039/B005537I](https://doi.org/10.1039/B005537I).
- (73) Hilf, J.; Frey, H., Propargyl-Functional Aliphatic Polycarbonate Obtained from Carbon Dioxide and Glycidyl Propargyl Ether. *Macromol. Rapid Commun.* **2013**, *34* (17), 1395-1400. <https://doi.org/10.1002/marc.201300425>.
- (74) Zhang, J.-F.; Ren, W.-M.; Sun, X.-K.; Meng, Y.; Du, B.-Y.; Zhang, X.-H., Fully Degradable and Well-Defined Brush Copolymers from Combination of Living CO<sub>2</sub>/Epoxide Copolymerization, Thiol-Ene Click Reaction and ROP of ε-caprolactone. *Macromolecules* **2011**, *44* (24), 9882-9886. [10.1021/ma202062g](https://doi.org/10.1021/ma202062g).
- (75) Darenbourg, D. J.; Tsai, F.-T., Postpolymerization Functionalization of Copolymers Produced from Carbon Dioxide and 2-Vinylloxirane: Amphiphilic/Water-Soluble CO<sub>2</sub>-Based Polycarbonates. *Macromolecules* **2014**, *47* (12), 3806-3813. [10.1021/ma500834r](https://doi.org/10.1021/ma500834r).
- (76) Yi, N.; Chen, T. D.; Unruangsri, J.; Zhu, Y.; Williams, C. K., Orthogonal functionalization of alternating polyesters: selective patterning of (AB)<sub>n</sub> sequences. *Chem. Sci.* **2019**, *10* (43), 9974-9980. [10.1039/C9SC03756J](https://doi.org/10.1039/C9SC03756J).
- (77) Plajer, A. J.; Williams, C. K., Heterocycle/Heteroallene Ring-Opening Copolymerization: Selective Catalysis Delivering Alternating Copolymers. *Angew. Chem. Int. Ed.* **2021**, *61*, e202104495. <https://doi.org/10.1002/anie.202104495>.
- (78) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H., Ring-Opening Metathesis Polymerization of Functionalized Cyclooctenes by a Ruthenium-Based Metathesis Catalyst. *Macromolecules* **1995**, *28* (18), 6311-6316. [10.1021/ma00122a043](https://doi.org/10.1021/ma00122a043).
- (79) Darenbourg, D. J.; Chung, W.-C.; Wilson, S. J., Catalytic Coupling of Cyclopentene Oxide and CO<sub>2</sub> Utilizing Bifunctional (salen)Co(III) and (salen)Cr(III) Catalysts: Comparative Processes Involving Binary (salen)Cr(III) Analogs. *ACS Catal.* **2013**, *3* (12), 3050-3057. [10.1021/cs4008667](https://doi.org/10.1021/cs4008667).
- (80) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A., Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties. *Macromolecules* **1994**, *27* (17), 4639-4647. [10.1021/ma00095a001](https://doi.org/10.1021/ma00095a001).
- (81) Graessley, W. W.; Edwards, S. F., Entanglement interactions in polymers and the chain contour concentration. *Polymer* **1981**, *22* (10), 1329-1334. [https://doi.org/10.1016/0032-3861\(81\)90231-7](https://doi.org/10.1016/0032-3861(81)90231-7).
- (82) Grijpma, D. W.; Penning, J. P.; Pennings, A. J., Chain entanglement, mechanical properties and drawability of poly(lactide). *Colloid. Polym. Sci.* **1994**, *272* (9), 1068-1081. [10.1007/BF00652375](https://doi.org/10.1007/BF00652375).
- (83) Pawlak, A., The Entanglements of Macromolecules and Their Influence on the Properties of Polymers. *Macromol. Chem. Phys.* **2019**, *220* (10), 1900043. <https://doi.org/10.1002/macp.201900043>.
- (84) Farah, S.; Anderson, D. G.; Langer, R., Physical and mechanical properties of PLA, and their functions in widespread applications — A comprehensive review. *Adv. Drug Deliv. Rev.* **2016**, *107*, 367-392. <https://doi.org/10.1016/j.addr.2016.06.012>.
- (85) Kang, Q.; Zhang, X.; Cui, Y.; Zhao, X.; Wang, W.; Zhang, J.; Zhang, Q.; Ma, L., Synthesis of high-density bio-jet fuel by one-pot Mannich-Michael reaction and subsequent hydrodeoxygenation over alkali-treated zeolite catalysts. *Fuel* **2023**, *349*, 128706. <https://doi.org/10.1016/j.fuel.2023.128706>.
- (86) Li, X.-L.; Deng, J.; Shi, J.; Pan, T.; Yu, C.-G.; Xu, H.-J.; Fu, Y., Selective conversion of furfural to cyclopentanone or cyclopentanol using different preparation methods of Cu-Co catalysts. *Green Chem.* **2015**, *17* (2), 1038-1046. [10.1039/C4GC01601G](https://doi.org/10.1039/C4GC01601G).
- (87) Neumann, S.; Leitner, L.-C.; Schmalz, H.; Agarwal, S.; Greiner, A., Unlocking the Processability and Recyclability of Biobased Poly(limonene carbonate). *ACS Sustain. Chem. Eng.* **2020**, *8* (16), 6442-6448. [10.1021/acssuschemeng.0c00895](https://doi.org/10.1021/acssuschemeng.0c00895).
- (88) Li, C.; van Berkel, S.; Sablong, R. J.; Koning, C. E., Post-functionalization of fully biobased poly(limonene carbonate): Synthesis, characterization and coating evaluation. *Eur. Polym. J.* **2016**, *85*, 466-477. <https://doi.org/10.1016/j.eurpolymj.2016.10.053>.
- (89) Peña Carrodegua, L.; González-Fabra, J.; Castro-Gómez, F.; Bo, C.; Kleij, A. W., AIII-Catalysed Formation of Poly(limonene)carbonate: DFT Analysis of the Origin of Stereoregularity. *Chem. - Eur. J.* **2015**, *21* (16), 6115-6122. <https://doi.org/10.1002/chem.201406334>.
- (90) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W., Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **2004**, *126* (37), 11404-11405. [10.1021/ja047258o](https://doi.org/10.1021/ja047258o).
- (91) Lamparelli, D. H.; Grimaldi, I.; Martínez-Carrión, A.; Bravo, F.; Kleij, A. W., Supercritical CO<sub>2</sub> as an Efficient Medium for Macromolecular Carbonate Synthesis through Ring-Opening Co- and Teroligomerization. *ACS Sustain. Chem. Eng.* **2023**, *11* (22), 8193-8198. [10.1021/acssuschemeng.3c02002](https://doi.org/10.1021/acssuschemeng.3c02002).
- (92) Wambach, A.; Agarwal, S.; Greiner, A., Synthesis of Biobased Polycarbonate by Copolymerization of Menth-2-ene Oxide and CO<sub>2</sub> with Exceptional Thermal Stability. *ACS Sustain. Chem. Eng.* **2020**, *8* (39), 14690-14693. [10.1021/acssuschemeng.0c04335](https://doi.org/10.1021/acssuschemeng.0c04335).
- (93) Arita, T.; Kayama, Y.; Ohno, K.; Tsujii, Y.; Fukuda, T., High-pressure atom transfer radical polymerization of methyl methacrylate for well-defined ultrahigh molecular-weight polymers. *Polymer* **2008**, *49* (10), 2426-2429. <https://doi.org/10.1016/j.polymer.2008.03.026>.
- (94) Kurtz, S. M., *UHMWPE biomaterials handbook: ultra high molecular weight polyethylene in total joint replacement and medical devices*. Academic press: 2009; <https://doi.org/10.1016/C2013-0-16083-7>.
- (95) Diodati, L. E.; Wong, A. J.; Lott, M. E.; Carter, A. G.; Sumerlin, B. S., Unraveling the Properties of Ultrahigh Molecular Weight Polyacrylates. *ACS Appl. Polym. Mater.* **2023**, *10.1021/acsp.3c02191*.
- (96) Hester, H. G.; Abel, B. A.; Coates, G. W., Ultra-High-Molecular-Weight Poly(Dioxolane): Enhancing the Mechanical Performance of a Chemically Recyclable Polymer. *J. Am. Chem. Soc.* **2023**, *145* (16), 8800-8804. [10.1021/jacs.3c01901](https://doi.org/10.1021/jacs.3c01901).

## Graphical Abstract

