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# Thermomorphic polyethylene-supported organocatalysts for the valorization of vegetable oils and CO<sub>2</sub>

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**Abstract:** A range of thermomorphic polyethylene-supported organocatalysts was prepared from *N*-alkyl imidazoles and polyethylene iodide (PE-I) with good yields (85-92%) and high functionality (98-99%). The catalytic activity of these species was studied for the ring-opening of epoxidized methyl oleate with CO<sub>2</sub> to give the corresponding cyclic carbonate. The reaction was carried out at 100°C to fully exploit the thermomorphic behaviour of the organocatalysts. The optimized conditions (neat, 100°C, 20 bar of CO<sub>2</sub>) were applied to a range of epoxidized fatty acids, including an epoxidized rapeseed oil, to give the corresponding carbonates with good yields (75-96%). The catalyst recycling was also studied and no significant loss of activity was observed after 10 runs. The fatty carbonates are important intermediates for the preparation of non-isocyanate polyurethanes (NIPUs).

## Introduction

CO<sub>2</sub> is currently the most important greenhouse gas since it is one of the main contributors to climate change.<sup>[1]</sup> The global CO<sub>2</sub> concentration is gradually increasing every year, reaching 412 ppm in the atmosphere in January 2020.<sup>[2]</sup> The rising concentration of CO<sub>2</sub> is mainly attributed to the consumption of fossil feedstock. The mitigation of greenhouse gases is one of the means to combat climate change and its impact, as stated in the 2030 United Nation's Sustainable Development Goals.<sup>[3]</sup> In this context, several strategies are currently pursued to mitigate CO<sub>2</sub> emissions.<sup>[4]</sup> On the one hand, CO<sub>2</sub> can be used as a non-toxic, abundant and cheap C1 building block in organic chemistry.<sup>[5]</sup> Indeed, it has already been used for decades for the industrial production of urea.<sup>[6]</sup> More recently, it has been demonstrated that CO<sub>2</sub> can be directly used for methylation<sup>[7]</sup> and carboxylation<sup>[8]</sup> of organic substrates and even for incorporation in heterocycles.<sup>[9]</sup> The insertion of CO<sub>2</sub> into epoxides is also an attractive transformation leading to organic carbonates with 100% atom economy. Organic carbonates have found numerous useful applications such as green solvents<sup>[10]</sup> and electrolytes for batteries.<sup>[11]</sup>

On the other hand, the use of renewable resources represents another opportunity for the limitation of CO<sub>2</sub> emissions.<sup>[12]</sup> Among the primary components of biomass, vegetable oils (triglycerides) are particularly attractive since they are cheap and widely available (about 204 Mt in 2018).<sup>[13]</sup> For instance, they

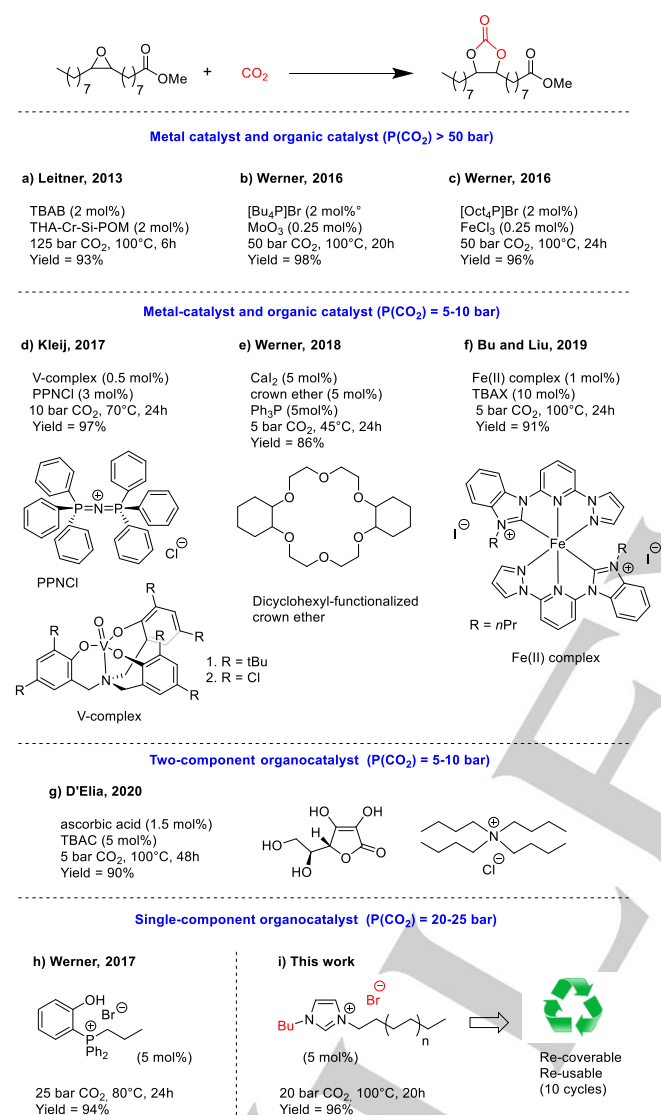
can be used as biofuel (biodiesel)<sup>[14]</sup> and for the production of valuable building-blocks.<sup>[15]</sup> The ring-opening of epoxidized fatty derivatives with CO<sub>2</sub> gives the corresponding cyclic carbonates and allows, at the same time, the utilization of renewable resources and the valorization of a waste. Moreover, fatty carbonates are excellent candidates for the formation of non-isocyanate polyurethanes (NIPUs).<sup>[16]</sup>

The ring-opening of epoxides with CO<sub>2</sub> has been extensively studied and the topic has been reviewed several times.<sup>[17]</sup> Metal-based catalysts<sup>[18-22]</sup> dominate the field in terms of catalytic activities, especially when combined with organic catalysts. Complementarily, organocatalysts can also be used to promote this transformation, mainly as single-component species.<sup>[23]</sup> Organic salts such as ammonium,<sup>[24]</sup> phosphonium,<sup>[25]</sup> and imidazolium<sup>[26]</sup> halides were originally used but new organocatalytic systems are also emerging such as polyols<sup>[27]</sup> and polyphenols,<sup>[28]</sup> DBU salts,<sup>[29]</sup> squaramides,<sup>[30]</sup> ascorbic acid,<sup>[31]</sup> and many more.<sup>[23, 32-33]</sup> Moreover, new metal-free catalysts are constantly being developed to provide recyclable systems, without compromising the catalytic efficiency.<sup>[34]</sup>

Generally, new catalytic systems (especially those operating under mild conditions) are developed using *terminal* epoxides as model substrates. Therefore, they are usually giving poor-to-moderate results when using *internal* epoxides such as fatty epoxides.<sup>[35]</sup> Indeed, these vegetable oil-derived epoxides are much more challenging substrates given that they are sterically hindered and pose solubility issues. That is the reason why, dedicated studies are usually necessary to efficiently convert fatty epoxides to carbonates using CO<sub>2</sub>.

In an early report, Wilkes *et al.* converted epoxidized soybean oil to cyclic carbonates by using tetrabutylammonium bromide (TBAB) as a catalyst at 110°C under a flow of CO<sub>2</sub>.<sup>[36]</sup> Similar conditions (TBAB, 100°C) were also reported by Doll and Erhan using fatty methyl esters under supercritical conditions ( $p(\text{CO}_2) = 103 \text{ bar}$ ).<sup>[37]</sup> To date, TBAB is the catalyst of choice for preparing fatty carbonates on the large scale, notably for their conversion to (poly)urethanes through aminolysis.<sup>[38]</sup> In order to find milder conditions, several groups have reported the use of metal catalysts to further activate the epoxides (Scheme 1). Leitner *et al.* have used TBAB as a catalyst in the presence of tetraheptylammonium silicochromium polyoxymethylene, THA-Cr-Si-POM.<sup>[39]</sup> It leads to 97% conversion of the epoxide with  $\geq 99\%$  of the carbonate but the reaction conditions were harsh

using 100°C under 125 bar of CO<sub>2</sub> (Scheme 1, a). Werner *et al.* developed another system using tetra-*n*-butylphosphonium bromide Bu<sub>4</sub>PBr in association with Molybdenum trioxide MoO<sub>3</sub>.<sup>[40]</sup> The use of this catalytic system at 100°C under 50 bar of CO<sub>2</sub> gave the desired carbonate in 98% yield (Scheme 1, b). In a continuous work, Werner *et al.* has substituted Bu<sub>4</sub>PBr with [Oct<sub>4</sub>P]Br and MoO<sub>3</sub> by Iron Chloride (III) FeCl<sub>3</sub> and obtained the corresponding carbonates with 96% yield under same reaction conditions (Scheme 1, c).<sup>[41]</sup>



**Scheme 1.** Reported catalytic systems for the preparation of cyclic carbonates from epoxidized methyl oleate and CO<sub>2</sub>.

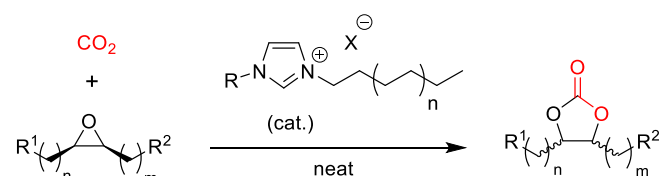
To reach high yields of fatty carbonates, the previous systems described require a very high pressure of CO<sub>2</sub> (50 and 125 bar) that could raise safety concerns. Other systems operating under mild conditions have also been described. Kleij *et al.* used a vanadium complex with bis(triphenylphosphine)iminium chloride PPNCl to selectively prepare cyclic carbonates (Scheme 1, d).<sup>[42]</sup> The reaction takes place at 70°C under 10 bar of CO<sub>2</sub> to give 97% yield of carbonate. Werner *et al.* developed a very effective

catalytic system consisting of calcium iodide (CaI<sub>2</sub>), dicyclohexyl-functionalized crown ether as a ligand and triphenylphosphine (Scheme 1, e). This three-component catalytic system gave 86% isolated yield of carbonates using very mild conditions (45°C, 5 bar CO<sub>2</sub>).<sup>[43]</sup> More recently, Bu and Liu have reported the use of iron(II) bispincer-type complexes in association with tetrabutyl ammonium halides (I, Br or Cl) (Scheme 1, f).<sup>[44]</sup> The catalytic system operates at 100°C under 5 bar of CO<sub>2</sub>. Interestingly, similar conditions (100°C, 5 bar of CO<sub>2</sub>) were recently reported by D'Elia using only a combination of two organocatalysts (ascorbic acid and TBAC) (Scheme 1, g).<sup>[45]</sup> Advantageously, the aforementioned catalytic systems operate under mild conditions. On the downside, mixtures of catalyst and co-catalyst(s) are necessary to reach such levels of performance, which leads to inherent difficulties for the catalyst recovery and re-use. The only example using a single-component organocatalyst was reported by Werner *et al.*<sup>[46]</sup> They used a hydroxy-functionalized phosphonium salt (5 mol%) at 80°C under 25 bar of CO<sub>2</sub> to give 94% yield of carbonate (Scheme 1, h). However, this organocatalyst could not be easily separated from the product, so its recycling has not been demonstrated in this context.

The recycling of catalysts is not always pertinent, notably when used to produce high value compounds for niche markets. On the contrary, it becomes of prime importance when used for high production volume chemicals presenting a lower added value. Considering that vegetable oil-based carbonates are mainly dedicated to the production of non-isocyanate polyurethanes, that could represent an important market in the future, it becomes evident that the use of recyclable catalysts is highly desirable.

In this context, we have recently reported the use of an organocatalyst supported on thermomorphic polyethylene<sup>[47]</sup> for the formation of cyclic carbonates from epoxides and CO<sub>2</sub>.<sup>[48]</sup> The benefit of such supported organocatalysts lies in the fact that they are homogeneous at high temperature and heterogeneous at room temperature. Therefore, they can offer both a high catalytic activity and a good recyclability. Considering our interest in the valorization of vegetable oils,<sup>[49]</sup> notably using organocatalysis,<sup>[50]</sup> we envisioned that such species could also be used as recyclable organocatalysts for the conversion of epoxidized fatty acid derivatives to biobased cyclic carbonates (Scheme 1, i).

Herein, we report the synthesis and characterization of several imidazolium organocatalysts supported on thermomorphic polyethylene for the preparation of cyclic carbonates from epoxidized fatty acid derivatives and CO<sub>2</sub> (scheme 2).

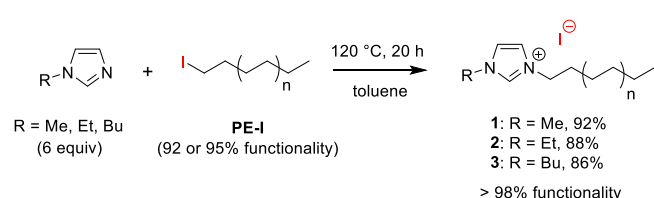


**Scheme 2.** Preparation of cyclic carbonates from epoxidized fatty acid derivatives and CO<sub>2</sub> using thermomorphic polyethylene-supported organocatalysts.

## Results and Discussion

### Synthesis of thermomorphic polyethylene-supported imidazolium salts.

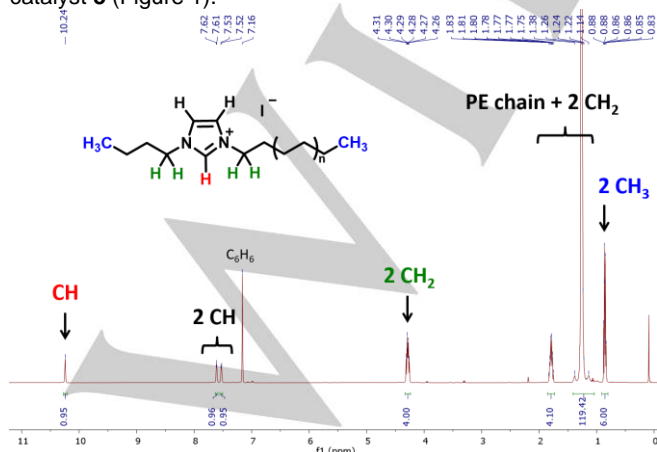
An iodine end-functionalized thermomorphic polyethylene (PE) precursor was first prepared on the 10-gram scale. Ethylene was polymerized by a controlled coordinative chain transfer polymerization using a dialkyl magnesium ( $\text{MgR}_2$ ) as chain transfer agent and a neodymium complex as a catalyst.<sup>[51]</sup> The resulting PE-Mg-PE was quenched with  $\text{I}_2$  to give polyethylene iodide (PE-I). Two batches were produced with a number average molar mass ( $M_n$ ) of  $1000 \text{ g}\cdot\text{mol}^{-1}$  and  $1200 \text{ g}\cdot\text{mol}^{-1}$  and with a functionality of 92% and 95%, respectively (determined by  $^1\text{H}$  NMR, the rest being mainly methyl terminated PE). Then, thermomorphic organocatalysts were synthesized from PE-I and 1-methyl-, 1-ethyl- and 1-butylimidazole. The reactions were carried out using 6 equivalents of the imidazole precursors in toluene at  $120^\circ\text{C}$  for 20 hours (Scheme 3).



**Scheme 3.** Synthesis of thermomorphic polyethylene-supported organocatalysts.

The complete conversion of PE-I was determined by  $^1\text{H}$ -NMR in each case. The imidazolium salts precipitated upon cooling and were collected by filtration. 3-Methyl-, 3-ethyl- and 3-butyl-1-polyethyleneimidazolium iodide **1-3** were obtained with 92%, 88% and 86% isolated yields, respectively. Surprisingly, the functionality was found to be > 98% for all catalysts, whatever the original functionality of the batch of PE-I used. This could be explained by the leaching of unfunctionalized PE, by differentiation between charged and neutral PE derivatives. Interestingly, about 80% of the excess of the imidazole precursors were recovered from the filtrate.

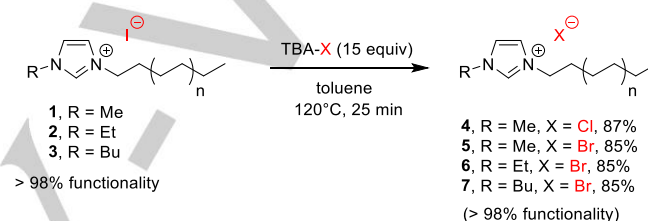
The catalysts were characterized by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR (see ESI for full details) and one example of  $^1\text{H}$  NMR is given here for catalyst **3** (Figure 1).



**Figure 1.**  $^1\text{H}$ -NMR (500 MHz, TCE/ $\text{C}_6\text{D}_6$  2:1/v/v, 363K, 128 scans) of PE-supported methyl imidazolium **3**. TCE: tetrachloroethylene.

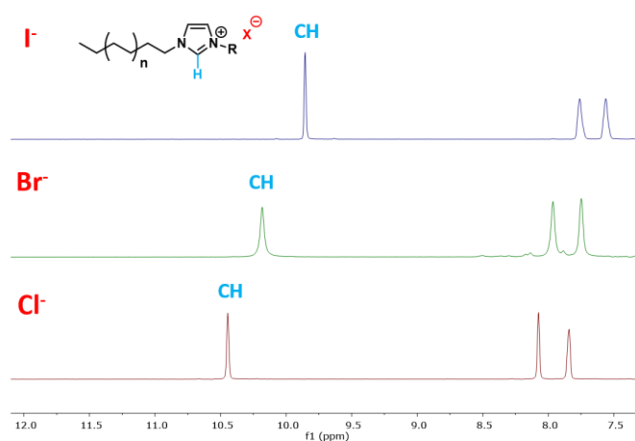
The characteristic signals at 10.24 ppm (red CH), 7.61 and 7.52 (black CHs) clearly indicate the presence of the acidic protons of the imidazolium core. All the other signals also confirm the grafting of the imidazole precursor onto the polyethylene support. The functionality of catalyst **3** was found to be > 98% by proton NMR, thus showing that all PE-I was converted to the desired compound. The polymerization degree,  $\text{DP}_n$  was found to be 30, thus giving a molar mass of  $M_n = 1100 \text{ g}\cdot\text{mol}^{-1}$  (Table 1, entry 3). The characteristics of the catalysts **1** and **2** are also gathered in Table 1 (entries 1-2).

In order to determine the effect of the counter-ion, an efficient ion exchange procedure was developed to exchange the iodine ion with chloride and bromide ion. The reaction was carried out starting from organocatalyst **1** at  $120^\circ\text{C}$  using TBAC and TBAB (Scheme 4).



**Scheme 4.** Synthesis of thermomorphic polyethylene-supported organocatalysts by ion-exchange procedure. TBA: tetrabutylammonium.

Under these conditions, 3-methyl-1-polyethyleneimidazolium chloride **4** and 3-methyl-1-polyethyleneimidazolium bromide **5** were obtained with 87% and 85% isolated yield, respectively. The ion exchange was proved by  $^1\text{H}$ -NMR from the shifting of the acidic proton from 9.8 ppm (I<sup>-</sup>), to 10.18 ppm (Br<sup>-</sup>) and 10.44 ppm (Cl<sup>-</sup>) (Figure 2).



**Figure 2.**  $^1\text{H}$ -NMR (500 MHz, TCE/ $\text{C}_6\text{D}_6$  2:1/v/v, 363K, 128 scans) of organocatalysts **4** and **5**. Zoom of the 7.3-12.1 ppm region. (R = Me). TCE: tetrachloroethylene. The measurement of the chemical shifts was performed at the same concentration for each catalyst (see ESI).

This shift also was observed for the less acidic protons of the imidazolium core. The same exchange procedure was repeated

starting from organocatalysts **2** and **3** bearing an ethyl and a butyl group on the imidazolium core, in order to exchange the iodide ion to a bromide. The corresponding organocatalysts **6** and **7** have been obtained both with 85% isolated yield (Scheme 4). All the other characteristics of the thermomorphic-polyethylene supported organocatalysts **1-7** are gathered in Table 1.

**Table 1.** Main characteristics of thermomorphic-polyethylene supported organocatalysts **1-7**.

Entry	Organocatalyst			Yield (%)	DP <sub>n</sub>	M <sub>n</sub> <sup>[a]</sup> (g.mol <sup>-1</sup> )
	R	X	N <sup>o</sup>			
1	Me	I	1	89	36	1260
2	Et	I	2	88	29	1040
3	Bu	I	3	85	30	1100
4	Me	Cl	4	87	37	1200
5	Me	Br	5	85	39	1270
6	Et	Br	6	85	29	990
7	Bu	Br	7	85	30	1000

[a] Calculated based on the <sup>1</sup>H NMR spectra. All functionalities were found to be > 98%.

### Thermomorphic polyethylene-supported organocatalyzed synthesis of cyclic carbonates from vegetable oils and CO<sub>2</sub>.

The catalytic activity of the new organocatalysts **1-7** was evaluated in the formation of cyclic carbonates from insertion of CO<sub>2</sub> into vegetable oil-based epoxides. The catalyst screening was first carried out using *cis*-epoxidized methyl oleate **8** as a model substrate and CO<sub>2</sub> to form the corresponding cyclic carbonate **9** (Table 2). Based on our previous results for the preparation of cyclic carbonates from internal epoxides and CO<sub>2</sub>,<sup>[48]</sup> the reactions were performed in solvent-free conditions at 100°C, under 20 bar of CO<sub>2</sub> for 20 hours using 4 mol% of the catalyst.

**Table 2.** Preliminary catalyst screening for the preparation of cyclic carbonates from epoxidized methyl oleate and CO<sub>2</sub>.<sup>[a]</sup>

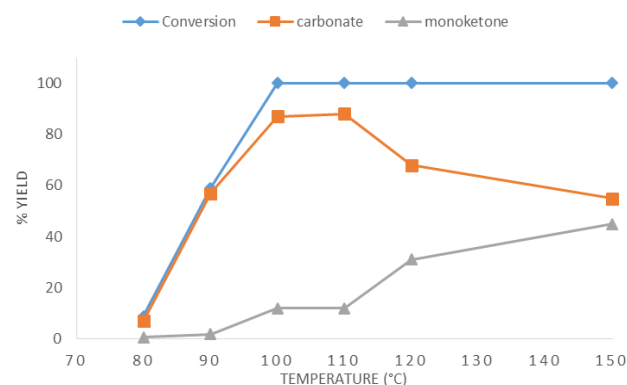
Entry	X	Conv. <sup>[a]</sup> <b>8</b> (%)	Yield <sup>[b]</sup> <b>9</b> (%)	Sel. <sup>[b]</sup> (%)	Cis/trans ratio <sup>[b]</sup>	Yield <sup>[b]</sup> <b>10</b> (%)
1	I	55	50	91	60:40	4
2	Cl	30	28	93	94:6	2
3	Br	> 99	86	87	55:45	12

1	I	55	50	91	60:40	4
2	Cl	30	28	93	94:6	2
3	Br	> 99	86	87	55:45	12

[a] Reaction conditions: 45-mL stainless steel autoclave, epoxide **8** (1.3 g, 4.16 mmol), catalyst **1**, **4** or **5** (4 mol%), 20 bar CO<sub>2</sub>, 20 hours. [b] Determined by GC and <sup>1</sup>H NMR.

Using catalyst **1** (with iodide), the conversion of epoxide **8** reached 55% and the corresponding carbonate **9** was formed with 50% yield, thus representing 91% selectivity with 60:40 *cis/trans* ratio (Table 2, entry 1). Ketone **10** was also obtained with 4% yield. This by-product is formed by a Meinwald rearrangement of epoxide **8**, as previously reported by others.<sup>[39,40,42]</sup> Then, using catalyst **4** (with chloride), both the conversion of **8** and the yield of **9** decreased to 30 and 28%, respectively (Table 2, entry 2). However, the *cis/trans* ratio reached 94:6 in this case. This result is consistent with those reported in the literature for catalytic systems using tetrabutylammonium chloride (TBAC) as a nucleophilic catalyst.<sup>[42-44]</sup> The established mechanism involves the stereospecific ring-opening of the epoxide by a nucleophilic anion, followed by addition of the formed alcoholate to CO<sub>2</sub> and subsequent ring-closure to form the carbonate.<sup>[41]</sup> The overall retention of configuration (from *cis*-epoxide to *cis*-carbonate) with TBAC was attributed to the poor leaving-group properties of the chloride anion, leading to a preferential S<sub>N</sub>2-like mechanism for the ring-closure of the carbonate. On the contrary, the bromide and iodide ions have much better leaving-group properties, thus preferentially forming a carbocation through a S<sub>N</sub>1-like mechanism, and finally producing a mixture of *cis*- and *trans*-carbonates. A full conversion of **8** was achieved using catalyst **5** (with bromide) and the desired carbonate **9** was formed in 86% yield and a 55:45 *cis/trans* ratio (Table 2, entry 3). However, in that case, the selectivity only reached 87% due to the formation of about 12% of ketone **10**. Noteworthy, when the reaction was carried out using catalyst **5** in the absence of CO<sub>2</sub>, the conversion of epoxide **8** only reached 15% and ketone **10** was obtained with 15% yield. Finally, the bromide ion was found to be the best due to the compromise between the nucleophilic character and the size of the anion, as previously reported by Leitner<sup>[39]</sup> and Werner.<sup>[40]</sup> So, from these results, thermomorphic polyethylene-supported organocatalyst **5** was selected for further optimization.

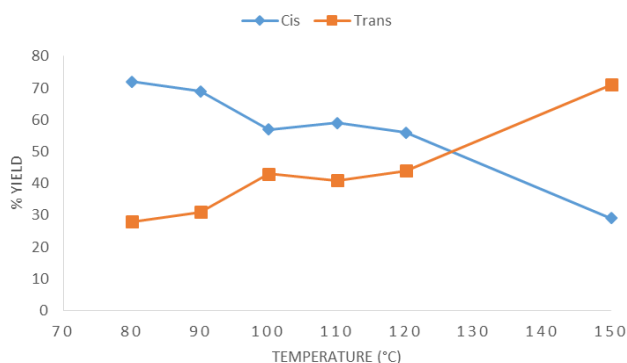
The effect of the temperature was next probe to achieve better selectivity (Figure 3).



**Figure 3.** Influence of the temperature. Reaction conditions: 45-ml stainless steel autoclave, epoxide **8** (1.3 g, 4.16 mmol), catalyst **5** (4 mol%), 20 bar CO<sub>2</sub>, 20 hours.

At 80°C, only a slight conversion of epoxide **8** was obtained (about 8%). Then, increasing the temperature to 90°C increases the conversion and the yield of carbonate reached 60%. A full conversion was observed at 100°C and the yield of carbonate **9** reached 87% in that case. This behavior was expected because the PE melting point is around 100°C, so the catalyst activity is quite low below this temperature. Increasing the temperature from 100°C to 150°C led to a decrease of yield of carbonate **9** (55% at 150°C), while the yield of ketone **10** increased to 44%. This could be explained by the fact that Meinwald rearrangement is favored at high temperature.

From this temperature study, a trend of *cis/trans* ratio was observed in which the formation of the *trans*-isomer is increasing with the increase temperature (Figure 4). We hypothesized that the increase of the temperature could enhance a S<sub>N</sub>1 pathway over a S<sub>N</sub>2 pathway. This could be also demonstrated by the increase in the yield of ketone **10** since the Meinwald rearrangement is favoured through a S<sub>N</sub>1 pathway. In addition, the *trans* carbonate production is enhanced by the S<sub>N</sub>1 mechanism.



**Figure 4.** Influence of ratio of the *cis*- and *trans*-isomer with the temperature. Reaction conditions: 45-ml stainless steel autoclave, epoxide **8** (1.3 g, 4.16 mmol), catalyst **5** (4 mol%), 20 bar CO<sub>2</sub>, 20 hours.

A temperature of 100°C was selected for further optimization (Table 3). The CO<sub>2</sub> pressure was increased to 30 bar at 100°C using catalyst **5** (Table 3, entry 1). Under these conditions, the conversion was complete and the yield of carbonates **9** increased to 92%. In order to keep moderate conditions, the pressure was maintained at 20 bar. Using catalyst **6** under 20 bar of CO<sub>2</sub> gave a lower yield (61%) but a higher 95% selectivity (Table 3, entry 2). Interestingly, catalyst **7** bearing a *n*-butyl chain gave a higher yield of carbonate **9** (85%) with an excellent 99% selectivity (Table 3, entry 3). We hypothesized that the nucleophilicity of bromide could be slightly increased by increasing the steric hindrance. Moreover, the solubility of the catalyst in the fatty epoxides could have been enhanced, especially as these reactions are run under solvent-free conditions. Satisfyingly, when the catalyst loading was increased to 5 mol%, the conversion was 98% and the yield of **9** reached 96%, thus giving a high 98% selectivity (Table 3, entry 4). These conditions were selected as the optimized conditions. A blank

experiment without catalyst gave only 5% conversion and 5% yield of carbonate **9**, thus showing the importance of the catalyst in this process (Table 3, entry 5).

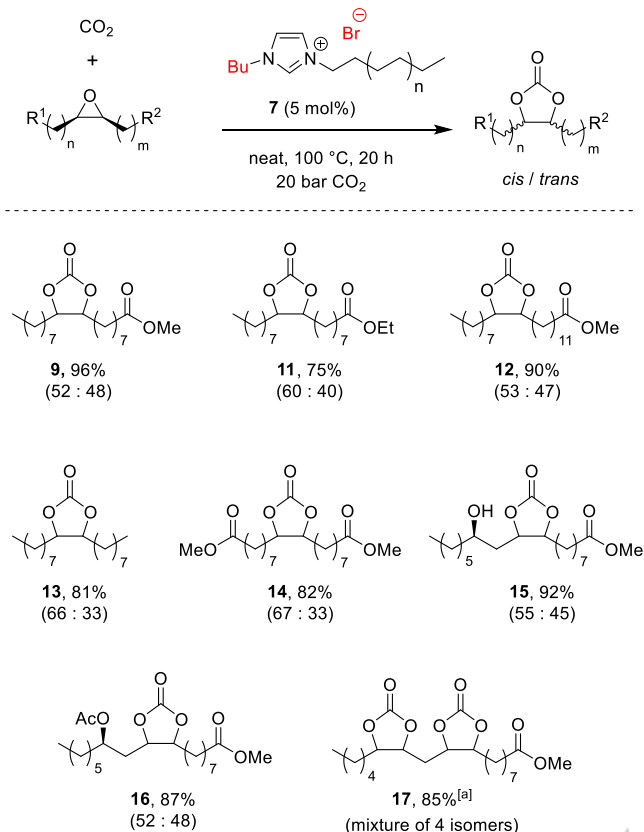
**Table 3.** Optimization of the reaction conditions.<sup>[a]</sup>

Entry	Catalyst	Conv. <sup>[a]</sup> <b>8</b> (%)	Yield <b>9</b> cis/trans ratio <sup>[b]</sup> (%)	Yield <sup>[b]</sup> <b>10</b> (%)	Sel. <sup>[b]</sup> <b>9</b> (%)
1 <sup>[c]</sup>	<b>5</b>	> 99	92 (52:48)	7	93
2	<b>6</b>	62	61 (72:28)	1	95
3	<b>7</b>	85	84 (65:35)	1	99
4 <sup>[d]</sup>	<b>7</b>	98	96 (60:40)	2	98
5	-	5	5 (95:5)	0	> 99
6	DBIB	74	68 (37:63)	6	92
7	TBAB	96	93 (57:43)	3	97

<sup>[a]</sup> Reaction conditions: 45-mL stainless steel autoclave, epoxide **8** (1.3 g, 4.16 mmol), catalyst **5-7** (4 or 5 mol%), 20 bar CO<sub>2</sub>, 20 hours. <sup>[b]</sup> Determined by GC and <sup>1</sup>H NMR. <sup>[c]</sup> P(CO<sub>2</sub>) = 30 bar. <sup>[d]</sup> 5 mol% of catalyst **7**. DBIB: 1,3-dibutyl-1*H*-imidazol-3-ium bromide. TBAB: tetrabutylammonium bromide.

For comparative purposes, the reaction was also performed with a non-supported version of the catalyst. When using 1,3-dibutylimidazolium bromide (DBIB), the conversion only reached 74% but the selectivity remains high (92%) (Table 3, entry 6). This result demonstrates that supporting such organocatalyst on a thermomorphic support is not deleterious for the catalytic activity, contrary to what is usually observed with insoluble supports. Even better, in our case, the supported organocatalyst is more active than its unsupported version, as already shown in our previous study.<sup>[48]</sup> Finally, the reaction was also performed with TBAB for further comparison. In that case, the conversion reached 96% and carbonate **9** was obtained with 93% yield (Table 3, entry 7). This result indicates that thermomorphic polyethylene-supported organocatalyst **7** has similar activity than TBAB, with the advantage of being recoverable and recyclable (*vide infra*).

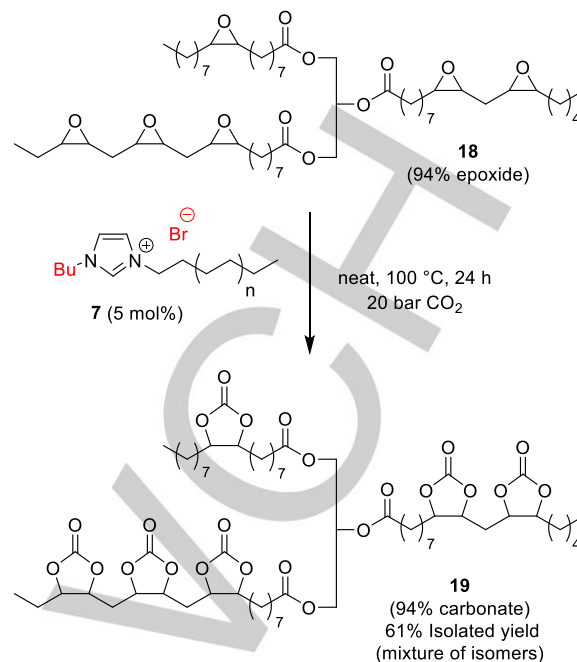
The scope of the reaction was investigated with a range of epoxides derived from fatty acid derivatives (Figure 5).



**Figure 5.** Scope of carbonated fatty acid derivatives obtained by thermomorphic polyethylene-supported organocatalyzed coupling of epoxides with CO<sub>2</sub>. Reaction conditions: 45-mL stainless steel autoclave, epoxide (1.3 g, 4.16 mmol), catalyst **7** (5 mol%), 20 bar CO<sub>2</sub>, 20 hours. The *cis/trans* ratio was determined by <sup>1</sup>H NMR on the crude reaction mixture. Isolated yields. <sup>[a]</sup> 5 mol% of catalyst / epoxide function.

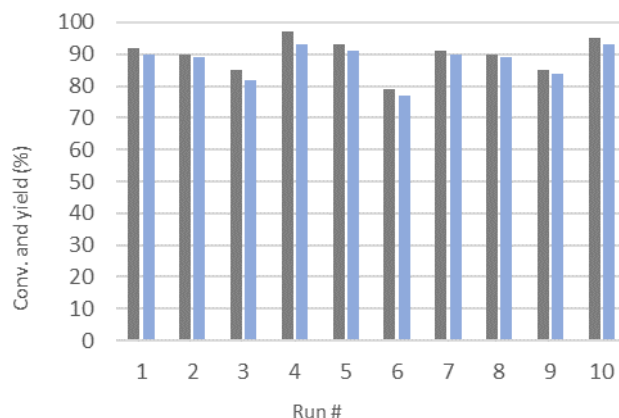
Repeating the reaction with epoxidized methyl oleate **8** under the optimized conditions gave carbonate **9** with 96% isolated yield after purification by column chromatography. Good yields (75–90%) were also obtained for carbonates **11** and **12** obtained from epoxidized ethyl oleate and methyl erucate, respectively. Symmetrical epoxides derived from the self-metathesis products of methyl oleate gave the corresponding carbonates **13** and **14** with 81 and 82% isolated yields. Methyl ricinoleate derivatives were next considered. With unprotected epoxidized methyl ricinoleate, carbonate **15** was obtained with 92% yield, while its OAc-protected version gave carbonate **16** with 87% yield. The reaction was also conducted with a bis-epoxide derived from methyl linoleate. In that case, bis-carbonate **17** was formed with 85% yield and was obtained as a mixture of 4 isomers.

Finally, in order to push forward this methodology, epoxidized rapeseed oil (94% epoxide content) was also subjected to the optimized conditions (Figure 6). After reaction, proton NMR has revealed that all epoxides were converted to the corresponding carbonates. Carbonated rapeseed oil was thus obtained with 94% carbonate content without any purification. Purification of the crude carbonated oil by column chromatography gave **19** with 61% yield. This result clearly demonstrates that the method is applicable to challenging substrates such as vegetable oils.



**Figure 6.** Formation of carbonated rapeseed oil **19** by thermomorphic polyethylene-supported organocatalyzed coupling of epoxidized rapeseed oil with CO<sub>2</sub>. Reaction conditions: 45-mL stainless steel autoclave, epoxide (1.57 g, 6 mmol of epoxide function), catalyst **7** (5 mol% per epoxide function), 20 bar CO<sub>2</sub>, 20 hours. The structure of the triglyceride is idealized and does not represent the proportions of each fatty acid.

Thanks to the unique properties of the thermomorphic polyethylene support, the organocatalyst crystallizes upon cooling the reaction mixture. Therefore, it could be recovered by filtration and re-used several times. So, the catalyst recycling was studied for the preparation of cyclic carbonate from epoxidized methyl oleate **8** and CO<sub>2</sub> as a model reaction (Figure 7).



**Figure 7.** Recycling studies. Reaction conditions: 45-mL stainless steel autoclave, epoxide **8** (1.3 g, 4.16 mmol), catalyst **7** (10 mol%), 20 bar CO<sub>2</sub>, 20 hours. The conversion and yield were determined by GC and <sup>1</sup>H NMR. Conversion of epoxide: gray, combined yields of carbonates (blue). The ratio of *cis/trans* carbonates varied from 13:87 to 22:78 over the runs.

The reaction was performed with 10 mol% of catalyst **7**. A conversion of 92% was reached for the first run and the desired

carbonate **9** was obtained with 90% yield. After reaction, the catalyst was precipitated by lowering the temperature, filtered, washed with EtOAc, dried and directly used without further purification. If some product is adsorbed on the catalyst, the catalyst could be recrystallized and the remaining product could be recovered from the filtrate. Satisfyingly, despite some variations in conversion (80-95%), the catalyst still performs well after 10 runs. This demonstrates that this single-component organocatalyst can be easily recovered and recycled without significant loss of activity.

## Conclusion

To conclude, we have reported here the synthesis of several thermomorphic polyethylene-supported imidazolium catalysts. The catalytic activity of these new species was evaluated for the insertion of CO<sub>2</sub> into epoxidized methyl oleate, used as a model substrate. It was shown that both the *N*-alkyl chain and the counter ion of the imidazolium affect the activity of the catalyst. After optimization of the reaction conditions, the conversion of the epoxide reached 98% and the desired carbonate was obtained with 96% yield. A range of epoxidized fatty acid derivatives, including an epoxidized rapeseed oil, was also converted to the corresponding carbonates with good yields (75-96%, 9 examples). Finally, the recycling studies showed that the catalyst could be recovered and recycled over 10 runs without significant loss of activity.

## Experimental Section

**General procedure for catalysts preparation.** *N*-Alkylimidazole (6 equiv), end-functionalized polyethylene iodide (92% or 95% functionality) and anhydrous toluene (10 mL, 0.05M) were introduced to a 100 ml round-bottom flask. The flask was equipped with a water condenser. The reaction mixture was heated at 120°C (oil bath) under argon atmosphere. After 20 hours, the reaction mixture was cooled down to 70°C, then EtOAc (40 ml) was added to solidify the product. The suspension was filtered on a membrane paper (0.1 µm). For better drying, the crude product could be washed with two portions of acetone (15 ml) or Et<sub>2</sub>O (15 ml). Then, the crude was recrystallized by dissolving in hot toluene (10 ml, 0.05 M). The resulting solution was cooled down to about 70°C, then EtOAc (30 ml) was added to precipitate the catalyst and filtered again on a membrane (0.1 µm) and washed with 2 portions of acetone (10 ml). The solid catalyst was dried in vacuum for 3 hours at 40°C.

**General procedure for ion exchange.** In a 100-ml round bottom flask, polyethylene-supported imidazolium iodide (0.4 mmol, 1 equiv), tetrabutylammonium chloride (TBACl, 6 mmol, 15 equiv.) or tetrabutylammonium bromide (TBAB, 6 mmol, 15 equiv.) and anhydrous toluene (4 ml, 0.05 M) were introduced. The flask was equipped with water condenser. The reaction mixture was heated at 120°C (oil bath) under argon atmosphere. After 25 minutes, the apparatus was cooled down to 70°C, then EtOAc (25 ml) was added to solidify the product and acetone (25 ml) was added to dissolve TBACl or TBAB. The slurry polymer was filtered on a paper membrane (0.1 µm) and washed with two portions of acetone (10 ml). Then, the crude was recrystallized by dissolving in hot toluene (10 ml, 0.05 M). The resulting solution was cooled down to about 70°C, then EtOAc (30 ml) was added to precipitate the catalyst and filtered again on a membrane (0.1 µm) and washed with 2 portions of acetone (10 ml). The solid was dried in a vacuum oven for 5 hours at 45°C to give the new catalyst as a white powder.

**Typical Procedure for insertion of CO<sub>2</sub> into epoxidized fatty acid derivatives.** Epoxidized methyl oleate **8** (1.30 g, 4.16 mmol) and catalyst **7** (0.215 g, 5 mol%, 98% functionality) were introduced into 45-ml autoclave with a magnetic stirrer, then the autoclave was purged 3 times with CO<sub>2</sub> to remove air. The autoclave was charged with CO<sub>2</sub> (20 bar) and heated to 100°C (oil bath) for 20 hours. Then, the autoclave was cooled to 0°C (ice bath), and CO<sub>2</sub> is released slowly before opening the autoclave to avoid any loss of materials. The crude reaction mixture was analyzed directly by GC and NMR.

**General procedure for recycling studies.** The recycling process was carried using catalyst **7** (0.47 g, 0.416 mmol, 10 mol%, Functionality 98%), with epoxidized methyl oleate **8** (1.30 g, 4.16 mmol, 98% purity) were introduced into 45-ml autoclave with a magnetic stirrer, then the autoclave was purged 3 times with CO<sub>2</sub> to remove air. The autoclave was charged with CO<sub>2</sub> (20 bar) and heated to 100°C (oil bath) for 20 hours. The autoclave was cooled to 0°C (ice bath), and CO<sub>2</sub> is released slowly before opening the autoclave to avoid any loss of materials. Then, EtOAc (40ml) was added into the crude mixture, then the suspension was filtered through paper membrane (0.1 µm), then washed with acetone (15ml). EtOAc was evaporated under reduced pressure to produce the pure desired product (87-90% Yield) and the solid catalyst collected was dried in oven for 3 hours at 50°C before reusing it without any further purification. The crude reaction mixture was analyzed directly by GC and NMR.

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## Conflict of Interest

The authors declare no conflict of interest.

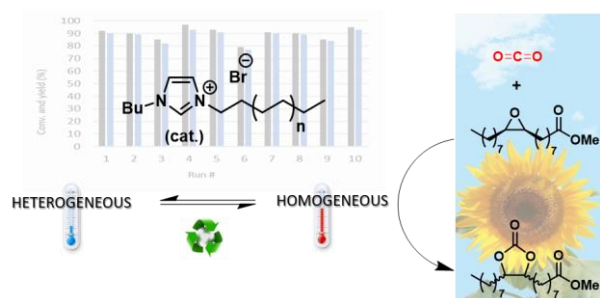
**Keywords:** Thermomorphic Polyethylene • Epoxides • Fatty Carbonates • Carbon dioxide • Organocatalysis.

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## Entry for the Table of Contents



Thermomorphic polyethylene-supported organocatalysts were used to catalyze the formation of carbonates from epoxidized fatty acid derivatives and CO<sub>2</sub>. Thanks to the thermomorphic behaviour of the polyethylene support, the organocatalysts exhibit similar catalytic activities than homogeneous organocatalysts and can also be recovered and reused for 10 cycles without significant loss of activity.

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