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Life Cycle Assessment for the Organocatalytic Synthesis of Glycerol Carbonate Methacrylate

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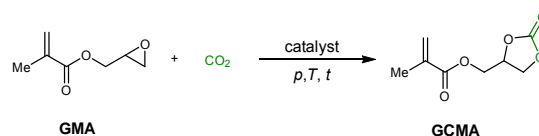
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Abstract: Bifunctional ammonium and phosphonium salts have been identified as potential organocatalysts for the synthesis of glycerol carbonate methacrylate (GCMA). Three of these catalysts showed high efficiency and allowed the conversion of glycidyl methacrylate with CO₂ to the desired product in >99% conversion and selectivity. Subsequently, immobilized analogues of selected catalysts were prepared and tested. A phenol-substituted phosphonium salt on a silica support proved to be a promising candidate for recycling experiments. The same catalyst was used in 12 consecutive runs, resulting in glycerol carbonate methacrylate yields up to 88% yield. Furthermore, a life cycle assessment was conducted for the synthesis of glycerol carbonate methacrylate starting from epichlorohydrin (EPH) and methacrylic acid (MAA). For the functional unit of 1 kg GCMA 15 wt.-% are attributed to the incorporation of CO₂ which led to a reduction of the global warming potential of 3% for the overall process.

Introduction

One of the major global challenges is the rising CO₂ concentration in the atmosphere which are mainly caused due to combustion of fossil resources for energy production.^[1] The most important strategy to address this issue is the reduction of CO₂ emissions through increased efficiency and alternative energy sources.^[2] Although the utilization of CO₂ cannot contribute to the immediate reduction of the CO₂ concentration, it has nevertheless become a fundamental aspect of the discussion on how to deal with CO₂ over the past 20 years.^[3] In this context, the chemical inertness of CO₂ is the most significant challenge for its utilization.^[4] Usually catalysts as well as high energy starting materials such as hydrogen or epoxides are required to convert CO₂ into value-added products. Already today CO₂ is used on industrial scale, e.g. in the synthesis of salicylic acid and urea. The production of urea is considered to be the largest CO₂-binding process with an annual production volume of about 150 Mt utilizing 109.5 Mt of CO₂.^[3e] Notably, the synthesis of

ammonia which is required for the production of urea, emits 153.9 Mt CO₂.^[5] Another example of utilization is the synthesis of methanol from CO₂ by hydrogenation.^[6] However, considering the carbon footprint of H₂ (currently 10–12 kg CO₂ per kg H₂)^[7] a sustainable access, e.g. from water splitting or electrolysis^[8] by using renewable energy is a prerequisite to realize environmentally and economically feasible processes. Hence, beside several other aspects in general, all necessary reagents and energy requirements need to be considered to assess an overall process in terms of sustainability and CO₂ savings.^[9] Despite numerous examples for the utilization of CO₂ as well as intensive research activities in this field, only a few approaches have provided a life cycle analysis^[10] (LCA) to prove their environmental benefit.^[11] The 100% atom economic synthesis of cyclic carbonates from epoxides and CO₂ is a highly active research area.^[12] The global production volume is about 80 kt per annum directly utilizing approximately 40 kt of CO₂.^[3f] However, the cyclic carbonate market is constantly growing mainly due to their interesting properties^[13] and broad range of applications, e.g. as green solvents,^[14] electrolytes^[15] or as additives in medicines and cosmetics.^[13] Moreover, The use of cyclic carbonates as intermediates in organic chemistry^[16] or monomers in polymer chemistry^[17] has also been explored. In the latter case the synthesis of glycerol carbonate methacrylate (GCMA) directly from glycidyl methacrylate (GMA) and CO₂ is of particular interest (Scheme 1). GMA can be prepared from epichlorohydrin and methacrylic acid.^[18] Alternative routes to GCMA are for example the esterification and transesterification of glycerol carbonate with methacrylate derivatives.^[13b, 19] Notably, both epichlorohydrin and glycerol carbonate can be obtained from glycerol as renewable feedstock.



Scheme 1. Synthesis of GCMA from GMA and CO₂.

GCMA is a promising monomer which has gained much interest for two main reasons:^[13b, 20] (1) its wide reactivity, allowing numerous applications, e.g. in conduction polymers^[21] and coatings^[22] (2) as useful option for the valorization of glycerol, which has become widely available as a major by-product from the manufacturing of biodiesel.^[23] Based on our expertise on the synthesis of cyclic carbonates from epoxides and CO₂,^[24] the organocatalytic production of GCMA was investigated and a LCA for the functional unit of 1 kg GCMA was carried out to estimate the carbon footprint.

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Results and Discussion

Based on our work with bifunctional onium salts as catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides we identified ammonium and phosphonium salts **1–4** as potential homogeneous catalysts for the synthesis of GCMA (Table 1).^[25] The bifunctional salts **1** and **2** are easily accessible by simple alkylation of *n*-tributyl phosphane^[25a] and *n*-tributyl amine^[25b] with iodoethanol, respectively, while **3** and **4** were prepared from 2-(diphenylphosphanyl)phenol^[25e] and benzyl or *n*-propyl bromide. GMA was converted with CO₂ under various reaction conditions in the presence of catalysts **1–4** to yield GCMA (Table 1). Excellent yields were achieved at 45°C after 18 h when 5 mol% of phosphonium salt **1** or ammonium salt **2** were employed, respectively (entries 1 and 2). In contrast catalysts **3** and **4** led to polymerization products under these conditions (entries 3 and 4). Notably, recently onium salts have been reported as polymerization catalysts for GMA.^[26] However, in the absence of a catalyst no conversion of GMA was observed at 45°C (entry 5). With regard to a production on industrial scale the space-time-yield needs to be considered. To improve the space-time-yield the reaction temperature was increased to 90°C and full conversion of GMA was achieved after 2 h even at lower catalyst loadings of 2 mol%.

Table 1. Evaluation of bifunctional organocatalysts **1–4** for the synthesis of GCMA from CO₂ and GMA.^[a]

Entry	Cat. [mol%]	<i>T</i> [°C]	<i>t</i> [h]	Conv. [%]	Sel. [%]	Yield GCMA [%]
1	1 (5)	45	18	>99	>99	99
2	2 (5)	45	18	>99	>99	>99
3	3 (5)	45	18	>99	–	– ^[b]
4	4 (5)	45	18	>99	–	– ^[b]
5	–	45	18	0	–	–
6	1 (2)	90	2	>99	>99	98
7	2 (2)	90	2	>99	>99	92
8	3 (2)	90	2	>99	–	– ^[b]
9	4 (2)	90	2	>99	99	99
10	–	90	2	0	–	–

[a] Reaction conditions: GMA (2.00 g, 14.1 mmol), 2 or 5 mol% catalyst, *T* = 45 or 90°C *p*(CO₂) = 1.0 MPa, *t* = 2 or 18 h. [b] An insoluble polymer was obtained.

Notably, at higher temperatures usually the formation of polymeric by-products was observed while in presence of **3** even at 90°C again only insoluble crosslinked polymer was obtained

(entry 8). The IR spectra of the polymer shows a carbonyl stretching vibration at 1784 cm⁻¹ for the carbonate indicating the incorporation of CO₂ as well as a band at 1723 cm⁻¹ for the ester group (compare Figure S10–S12).^[27] Thus, we further investigated the polymerization process by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Neat GMA proved to be stable up to its boiling point of 189°C (Figure S18).^[28] In contrast, the DSC diagram of neat GCMA show an exothermic reaction >90°C which can be addressed to the polymerization of GCMA (Figure S19).^[19a, 29] The formed polymer shows a glass transition temperature of 102°C. The curve of this polymer shows very similar characteristics compared to the DSC curve obtained from the polymer which is formed under the reaction conditions with catalyst **3** from entry 7 (Figure S20). This indicates the polymerization of the desired GCMA rather than the substrate GMA. The results from table 1 indicate that the polymerization strongly depends on the chosen reaction conditions (*t*, *T*) as well as on the catalyst. It has to be mentioned that in the absence of a catalyst no conversion was found at 90°C after 2 h (entry 10). In contrast, at temperatures ≥110°C polymerization of GMA is observed. However, bifunctional onium salts **1**, **2** and **4** gave the desired product in excellent yields up to 99% (entries 6, 7 and 9). These catalysts operate under comparatively mild reaction conditions in the absence of co-catalysts. Beside these advantages, the possibility of immobilization by simple quarternarization on suitable supports with the aim of facilitating catalyst recovery and recycling more easily is another attractive feature.^[25e, 30]

In this context the attention was turned to the utilization of immobilized catalysts **5–8** for the synthesis of GCMA from GMA and CO₂ (Table 2).

Table 2. Evaluation of immobilized bifunctional organocatalysts **5–8** for the synthesis of GCMA from CO₂ and GMA.^[a]

Entry	Cat. [mol%]	<i>T</i> [°C]	<i>T</i> [h]	Conv. [%]	Sel. [%]	Yield GCMA [%]
1	5 (5)	45	18	40	>99	40
2	5 (2)	90	2	67	>99	67
3	5 (2)	90	6	75	93	70 ^[c]
4 ^[b]	5 (2)	100	1	>99	81	81 ^[c]
5	6 (5)	45	18	90	>99	90
6	6 (2)	90	2	91	>99	91

7	6 (2)	90	6	>99	>99	>99
8	7 (2)	90	2	95	–	– ^[c]
9	8 (2)	90	2	90	>99	90
10	8 (2)	90	6	>99	>99	>99

[a] Reaction conditions: GMA (2.00 g, 14.1 mmol), 2 or 5 mol% catalyst, $T=45\text{--}100^\circ\text{C}$ $p(\text{CO}_2)=1.0\text{ MPa}$, $t=2\text{--}18\text{ h}$. [b] $p(\text{CO}_2)=4.0\text{ MPa}$. [c] An insoluble polymer was obtained.

These catalysts can be easily prepared by converting triethanol amine or (2-hydroxyphenyl)-diphenyl-phosphane with the respective commercially available functionalized supports. The conversion of GMA in the presence of 5 mol% **5** at 45°C gave the desired product in a moderate yield of 40% after 18 h (entry 1). Increasing the reaction temperature to 90°C led to a yield of 67% and 92% after 2 and 6 h, respectively even at lower catalyst loadings of 2 mol% (entries 2 and 3). At higher reaction temperatures (100°C) and pressure (4.0 MPa), the formation of insoluble polymeric by-product was observed and GCMA was obtained in 81% after 1 h (entry 4). The polystyrene-based catalyst **6** showed significantly higher GCMA yields at both 45°C and 90°C compared to the silica-bound catalyst **5** (entry 5 vs. 1 and 6 vs. 2). Full conversion of GMA to GCMA was obtained in the presence of 2 mol% **6** after 6 h (entry 7). In contrast polystyrene-supported catalyst **7** led to complete polymerization (entry 8), which corresponds to the result of the homogeneous analog **3** (Table 2, entry 7). Also in this case the IR spectrum shows bands for carbonyl vibrations at 1786 cm^{-1} and 1724 cm^{-1} respectively for the carbonate and ester. In the presence of silica-supported phosphonium bromide **8** the desired cyclic carbonate was obtained in 90% yield after 2 h at 90°C and a CO_2 pressure of 1.0 MPa (entry 9). Under otherwise identical reaction conditions, this yield was improved to >99% by increasing the reaction time to 6 h (entry 10). Considering the similar activities of catalysts **6** and **8** as well as the fact that silica supports usually show higher stability against mechanical stress compared to polystyrene supports we choose catalyst **8** for catalyst recovery and recycling studies.^[25e, 30c, 31]

We intended to reveal any catalyst deactivation quickly and thus performed the recycling experiments employing 2 mol% of **8** at 90°C , 1.0 MPa and 2 h. Under these conditions catalyst **8** resulted in a conversion of 90% with an excellent selectivity of >99% (Table 2, entry 9). In accordance with the results of the catalyst testing, an isolated yield of 88% of GCMA was obtained in the first run (Figure 1).

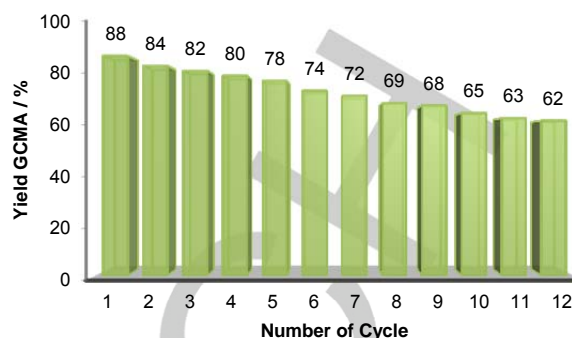
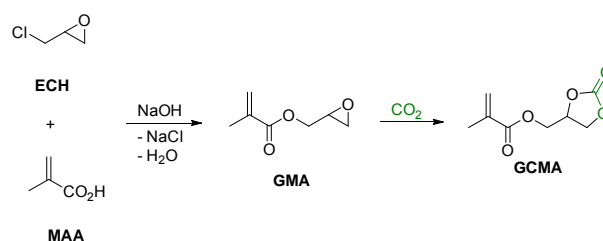


Figure 1. Recycling of the immobilized catalyst **8** in the synthesis of GCMA from GMA and CO_2 . Reaction conditions: GMA (2.00 g, 14.1 mmol), 2 mol% **8**, 90°C $p(\text{CO}_2)=1.0\text{ MPa}$, $t=2\text{ h}$. Isolated yields are given.

Subsequently, the GCMA yield decreased successively below 80% in the 5th run down to 62% in run 12. This indicates a partial catalyst deactivation during the recycling process which can be addressed to 1) loss of catalyst due to mechanical stress and leaching, 2) formation of a polymer film on the catalyst surface and/ or 3) anion exchange during the isolation/washing.^[25e] This is supported by a total catalyst loss of 21% and a decrease of 26% in the Br^- content. The experimental work on the synthesis of GCMA was accompanied by Life Cycle Assessment calculations in order to determine the impact of CO_2 utilization to the carbon footprint of the functional unit of 1 kg GCMA. Recently, Cucciniello, Cespi and co-workers nicely showed the advantages of LCAs in the early stage method development e.g. in the synthesis of monoalkyl glyceryl ethers from glycidol and glycerol.^[32] Herein the carbon footprint was determined in CO_2 -equivalents according to the global warming potential (GWP) as inherent part of CML2001 methodology in licensed software GaBi 5. All calculations were performed based on common ISO standards (ISO 14040 and ISO 14044).^[27] The LCA calculations for the cradle-to-gate analysis are based on an ASPEN simulation and the corresponding flow sheets are depicted in the supporting information. The synthesis of GCMA starts with the conversion of epichlorohydrin (ECH) and methacrylic acid (MAA) to GMA and the subsequent insertion of CO_2 to GMA producing the desired GCMA (Scheme 2).^[18]



Scheme 2. Synthetic approach for the synthesis of glycidyl methacrylate (GMA) from epichlorohydrin (ECH) and methacrylic acid (MAA) and subsequent conversion with CO_2 to glycerol carbonate methacrylate (GCMA).

The carbon footprint estimation (CFE) for this process is shown in Figure 2. The gravimetric CO₂ content in GCMA is approximately 15 wt.% (148 g of CO₂ are incorporated in 1 kg of GCMA). However, the major CO₂ burden is related to the starting materials. 3.04 kg CO₂-equiv is connected to the synthesis of ECH and 1.48 kg CO₂-equiv to MAA for the production of 1 kg GCMA. This accounts for 93% of the total global warming potential (GWP).

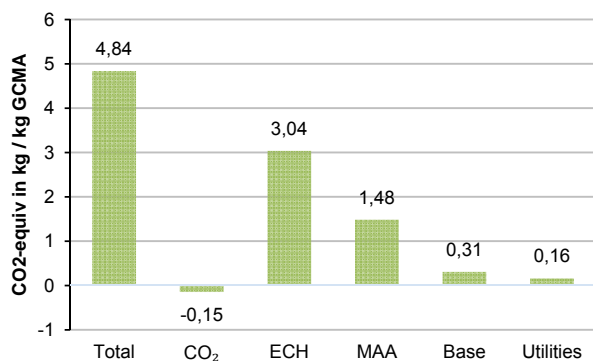


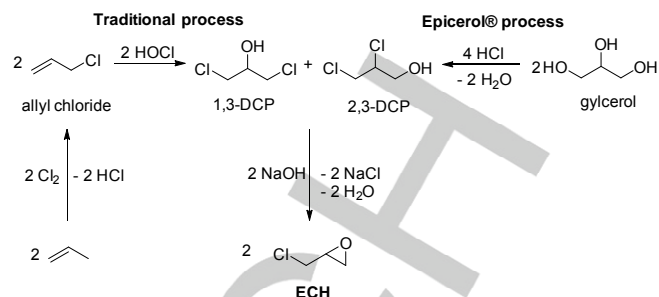
Figure 2. The total GWP of the overall process as well the contribution of the single shares of the raw materials, base and utilities burdens and CO₂ benefit are depicted.

Minor contributions to the GWP can be attributed to the sodium hydroxide (base) and utilities such as electricity, process steam, water and waste water treatment. Thus, the overall emissions amount to 4.99 kg CO₂-equiv per 1 kg of product which is reduced by 3% (0.15 kg CO₂-equiv/ 1 kg product) due to the incorporation of CO₂.

Obviously, the raw materials ECH and MAA have the most significant impact on the total GWP. Initially we considered the use of ECH obtained from chlorohydrin process. Herein fossil-based propene is reacted in two steps to allyl chloride and subsequently converted to ECH (Scheme 3).^[33] Since ECH has the highest contribution to the GWP we also considered alternative sources of this starting material. In this context we considered the use of bio-based ECH produced from glycerol by the EPICEROL® process.^[34] Glycerol is widely available as a major by-product from the biodiesel production. The so-called "biodiesel" is a popular term for the fatty acid methyl esters formed by transesterification of vegetable oils with methanol.^[33, 35]

Table 3. Other LCA criteria for the synthesis of 1 kg GCMA.^[a]

Entry	Category	
1	Abiotic Depletion (ADP elements) [kg Sb-equiv.]	1.78·10 ⁻⁵
2	Acidification Potential (AP) [kg SO ₂ -equiv.]	9.70·10 ⁻³
3	Eutrophication Potential (EP) [kg Phosphate-equiv.]	1.45·10 ⁻³
4	Freshwater Aquatic Ecotoxicity Potential (FAETP inf.) [kg DCB-equiv.]	8.37·10 ⁻³
5	Global Warming Potential (GWP 100 years) [kg CO ₂ -equiv.]	4.84
6	Human Toxicity Potential (HTP inf.)	9.81·10 ⁻²



Scheme 3. Petroleum-based (traditional Process) route to ECH starting from propene and bio-based Epicerol® process starting from glycerol.^[33]

Notably, if bio-based ECH produced by the EPICEROL® process is considered for the synthesis of GCMA the total emission is reduced by 47% from 4.84 to 2.55 kg CO₂-equiv per 1 kg GCMA (Figure 3). This clearly indicates the benefit of LCA and CFE when evaluating a process since not only the incorporated amount of CO₂ in the product has to be considered but the emissions and savings of the overall process. Beside the GWP, ten additional criteria within the LCA and the primary energy demand have been evaluated for this new process based on the traditional process starting from propene. The obtained values for these other categories are shown in Table 3.

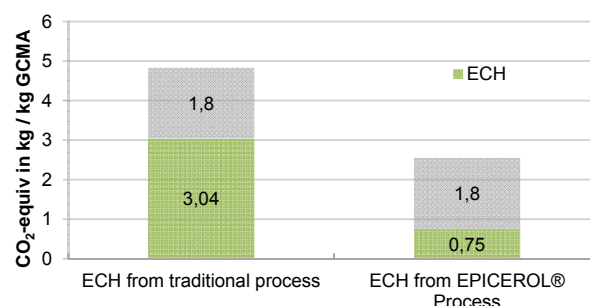


Figure 3. Total GWP for the synthesis of GCMA utilizing ECH from allyl chloride (traditional process) or from glycerol (EPICEROL® process). The green bar indicates the contribution of ECH on the GWP depending on the source. The grey bar indicates the sum of all other contributions (MAA, base, utilities) to the GWP.

	[kg DCB-equiv.]	
7	Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB-equiv.]	242.17
8	Ozone Layer Depletion Potential (ODP, steady state) [kg R11-equiv.]	5.93·10 ⁻⁸
9	Photochem. Ozone Creation Potential (POCP) [kg Ethene-equiv.]	1.28·10 ⁻²
10	Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB-equiv.]	6.33·10 ⁻³
11	Primary energy demand from renewable and non-renewable resources (net. calculated value) [MJ]	102.49

[a] Source CML2001 database, year 2010.

Conclusions

Glycerol carbonate methacrylate was prepared from glycidyl methacrylate and CO₂ in the presence of bifunctional phosphonium and ammonium salts as homogeneous organocatalysts. Yields >90% of the desired product were obtained after short reaction times of 2 h at 90°C. Immobilized analogs of selected catalysts were prepared and tested as potentially recyclable catalysts. The silica supported bifunctional phosphonium salt gave the desired product in >99% yield after 6 h at 90°C. DSC and TGA studies revealed that GCMA rather than GMA is prone to polymerization depending on the reaction conditions and employed catalyst. Subsequently, a recycling study was performed and the catalysts was recovered and reused in 12 consecutive runs. In the recycling experiments the reaction time was reduced to 2 h to reveal possible catalyst deactivation. During the recycling process the yield dropped gradually with each run from 88% in run 1 to 62% in the 12th run. The partial deactivation might be addressed to ion exchange e.g. due to traces of water, catalyst leaching and mechanical stress. This study was accompanied by a cradle-to-gate life cycle assessment for the synthesis of glycerol carbonate methacrylate (GCMA) from epichlorohydrin (ECH), methacrylic acid (MAA) and CO₂ in two steps. Interestingly, the LCA revealed a potential saving of 3% of CO₂-equivalents/ greenhouse gas emissions due to the incorporation of CO₂ into the product in the overall process. At first this seems to be surprising due to the fact that the CO₂ content in GCMA is approximately 15 wt.% (148 g of CO₂ are incorporated into 1 kg of GCMA). However, major contribution to the emission of greenhouse gases can be addressed to the reactants ECH and MAA which are accountable for over 90% of the total GWP. Notably, if bio-based ECH produced by the EPICEROL[®] process is considered for the synthesis of GCMA the total emission could be reduced by 47%.

Experimental Section

Synthesis of the homogeneous catalysts 1–4

Tri-*n*-butyl-(2-hydroxyethyl)phosphonium iodide (**1**)^[25c]

A mixture of tri-*n*-butylphosphine (1.62 g, 8.00 mmol) and 2-iodoethanol (1.43 g, 8.31 mmol) were stirred for 24 h at 60°C. The crude product was washed with Et₂O (3×5 mL). After removal of all volatiles in vacuo the product **1** (2.96 g, 7.91 mmol, 99%) was obtained as a colorless solid. ¹H

NMR (300 MHz, CDCl₃) δ = 0.97 (t, ³J_{H,H} = 7.0 Hz, 9H), 1.47–1.65 (m, 12H), 2.32–2.42 (m, 6H), 2.73 (dt, ³J_{H,P} = 11.7 Hz, ³J_{H,H} = 5.9 Hz, 2H), 4.12 (dt, ²J_{H,P} = 20.6 Hz, ³J_{H,H} = 5.5 Hz, 2H), 4.30 (br. s, 1H, OH) ppm.

Tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide (**2**)^[25b]

A mixture of tri-*n*-butylamine (1.77 g, 9.57 mmol) and 2-iodoethanol (1.59 g, 9.23 mmol) were stirred for 24 h at 80°C. Subsequently the reaction mixture was washed with Et₂O (3×5 mL). After removal of all volatiles in vacuo product **2** (2.79 g, 7.81 mmol, 85%) was obtained as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 1.03 (t, ³J = 7.3 Hz, 9H), 1.40–1.52 (m, 6H), 1.64–1.75 (m, 6H), 3.39–3.44 (m, 6H), 3.59 (t, ³J = 4.7 Hz, 2H), 4.13–4.19 (m, 2H), 4.47 (t, ³J = 6.1 Hz, 1H, OH) ppm.

Benzyl-(2-hydroxyphenyl)diphenylphosphonium bromide (**3**)^[25e]

A mixture of 2-(diphenylphosphanyl)phenol (500 mg, 1.80 mmol) and benzyl bromide (1.54 g, 8.98 mmol) were stirred at 110°C for 24 h. Subsequently the product was precipitated from CH₂Cl₂ and washed with EtOAc (3×10 mL) Et₂O (3×5 mL). After removal of all volatiles in vacuo product **3** (640 mg, 1.42 mmol, 79%) was obtained as a colorless solid. ¹H NMR (300 MHz, CDCl₃): δ = 4.59 (s, 1H), 4.64 (s, 1H), 6.68–6.76 (m, 1H), 6.85–6.91 (m, 1H), 7.01–7.05 (m, 2H), 7.15–7.40 (m, 7H), 7.49–7.60 (m, 5H), 7.68–7.73 (m, 2H), 8.15–8.20 (m, 2H), 11.39 (s, 1H) ppm.

(2-Hydroxyphenyl)diphenyl(propyl)phosphonium bromide (**4**)^[25e]

A mixture of 2-(diphenylphosphanyl)phenol (916 mg, 3.28 mmol) and 1-bromopropane (2.02 g, 16.4 mmol) was stirred at 110°C for 18 h. Subsequently the reaction mixture was washed with Et₂O (4×10 mL). After removal of all volatiles in vacuo product **4** (1.14 g, 2.84 mmol, 87%) was obtained as a colorless solid. ¹H NMR (300 MHz, CDCl₃): δ = 1.08–1.13 (m, 3H), 1.62–1.78 (m, 2H), 3.07–3.17 (m, 2H), 6.80–6.95 (m, 2H), 7.51–7.65 (m, 9H), 7.71–7.78 (m, 2H), 8.05–8.10 (m, 1H), 11.07 (s, 1H) ppm.

General procedure for the screening of homogeneous 1–4:

A 45 cm³ stainless steel autoclave was charged with 2 or 5 mol% catalyst 1–4 and GMA (2.00 g, 14.1 mmol). The reactor was sealed and charged with 1.0 MPa CO₂ at 23°C until the equilibrium was reached. The reaction mixture was stirred for 2 or 18 h at 45 or 90°C. Subsequently, the reactor was cooled to ≤20°C with an ice bath and CO₂ was released slowly. The reaction mixture was diluted with CH₂Cl₂ and filtered over a short silica plug. After removal of all volatiles in vacuo the yield of GCMA was determined and the purity of the product verified by GCMS and ¹H NMR.

Synthesis of the immobilized catalysts 5–8

Synthesis of silica supported catalysts (**5**)^[30c]

A mixture of aminopropyl functionalized silica gel (1.00 g, 1 mmol·g⁻¹ N-loading) and 2-iodoethanol (5.00 g, 29.1 mmol) were mixed in a shaking device at 60°C under argon for 4 d. The obtained solid was filtered off, washed with Et₂O (8×20 mL) and dried in vacuum to yield **5** (1.24 g) as a yellow solid. ¹³C NMR (solid state) δ= 5–12 (CH₂, br.); 13–22 (CH₂, br.); 45–50 (CH₂, br.); 51–59 (CH₂, br.); 61–63 (CH₂, br.); 64–66 (CH₂, br.) ppm; Elemental Analysis: Calculated after alkylation N 1.10%, found N 0.94%, (0.68 mmol g⁻¹ N-loading).

Synthesis of polystyrene supported catalysts (**6**)^[30c]

A mixture of diethanolamino polystyrene (1.20 g, 1.6 mmol·g⁻¹ N-loading) and 2-iodoethanol (14.6 g, 84.9 mmol) were mixed in a shaker under argon at 60°C for 4 d. The obtained solid was filtered off, washed with Et₂O (8×20 mL) and dried in vacuum to yield **6** (1.41 g) as a yellow solid. ¹³C NMR (solid state) δ= 6–16 (CH₂, br.); 21–53 (CH₂, br.); 60–66 (CH₂, br.) 121–138 (br.); 140–150 (br.); 220–237 (br.); 240–248 (br.) ppm; Elemental Analysis: found N 1.65%, (1.18 mmol·g⁻¹ N-loading).

Synthesis of polystyrene-supported catalyst (**7**)^[25e]

A mixture of polystyrene-supported benzyl bromide (1.00 g, 2.96 mmol·g⁻¹, 1.00 equiv) and the 2-(diphenylphosphanyl)phenol (1.65 g, 5.93 mmol, 2.00 equiv) were mixed in a shaking device for 96 h at 110°C in toluene under an argon atmosphere. The crude product was washed with Et₂O (4×20 mL). After removal of all volatiles in vacuo catalyst **7** (0.67 g) was obtained as white solid.

¹³C NMR (solid state) δ= 3–55 (CH₂, br.), 110–137 (Ar, br.), 138–154 (Ar, br.), 155–168 (br.), 220–256 (br.) ppm. ³¹P NMR (solid state) δ= -60–23 (br.), 1–52 (br.), 69–110 (br.) ppm; Elemental Analysis: found Br 5.59%, (0.70 mmol g⁻¹ Br-loading).

Synthesis of silica supported catalyst (**8**)^[25e]

A mixture of 4-bromopropyl-functionalized silica gel (1.00 g, 1.50 mmol·g⁻¹ Br-loading, 1.00 equiv) and the 2-(diphenylphosphanyl)phenol (840 mg, 3.00 mmol, 2.00 equiv) were mixed in a shaking device for 4 d at 110°C in 2 mL toluene under an argon atmosphere. The crude product was washed with Et₂O (4×20). Subsequently, all volatiles were removed in vacuo to yield **8** (1.13 g) as white solid.

¹³C NMR (solid state) δ= -5–6 (CH₂, br.), 6–65 (CH₂, br.), 92–109 (Ar, br.), 110–122 (Ar, br.), 122–145 (br.), 153–164 (br.), 207–236 (br.) ppm. ³¹P NMR (solid state) δ= -53–19 (br.), 1–33 (br.), 33–43, 68–100 (br.) ppm. Elemental Analysis: found Br 6.36%, (0.80 mmol g⁻¹ Br-loading), Elemental Analysis after Run 12: found Br 6.36%, (0.80 mmol g⁻¹ Br-loading).

General procedure for the screening of immobilized catalysts 5–8

A 45 cm³ stainless steel autoclave was charged with 2 or 5 mol% catalyst **5–8** and GMA (2.00 g, 14.1 mmol). The reactor was sealed and charged with 1.0 MPa CO₂ at 23°C until the equilibrium was reached. The reaction mixture was stirred for 2 or 18 h at 45 or 90°C. Subsequently, the reactor was cooled to ≤20°C with an ice bath and CO₂ was released slowly. The reaction mixture was removed by extraction with Et₂O (3×3 mL). After removal of all volatiles in vacuo the yield of GCMA was determined and the purity of the product verified by GCMS and ¹H NMR.

General procedure for recycling experiments

A 45 cm³ stainless steel autoclave was charged with catalyst **8** (0.02 equiv.) and GMA (2.00 g, 14.7 mmol, 1.0 equiv). The reactor was sealed and charged with 1.0 MPa CO₂ at 23°C until the equilibrium was reached. Subsequently, the reactor was heated to 90°C while p(CO₂, 90°C) was kept constant at 1.0 MPa. After 2 h the reactor was cooled to ≤20°C with an ice bath and CO₂ was released slowly. The reaction mixture was removed from the immobilized catalyst by washing with Et₂O (3×3 mL) and dried in a desiccator in vacuo for at least 2 h and reused. After removal of all volatiles from the organic layer in vacuo the yield of GCMA was determined. ¹H NMR (300 MHz, CDCl₃): δ= 1.89–1.90 (m, 3H), 4.24–4.41 (m, 3H), 4.53–4.58 (m, 1H), 4.93–5.00 (m, 1H), 5.59–5.61 (m, 1H), 6.08–6.09 (m, 1H) ppm.

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Life Cycle Assessment for the
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Homogeneous & immobilized organocatalysts for the synthesis of glycerol carbonate methacrylate and life cycle assessment