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Highly Efficient Polymer-Supported Catalytic System for the Valorization of Carbon Dioxide

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Polydibenzo-18-crown-6 was utilized as a co-catalyst and polymeric support in combination with potassium iodide for the synthesis of cyclic carbonates from carbon dioxide and epoxides under mild and solvent-free conditions. The efficiency of this catalytic system can be easily increased by loading the polymer with KI prior to the reaction. The influence of various reaction parameters were studied thoroughly. The scope and limitation of the catalyst system was studied at 80 °C and 100 °C. A large number of terminal epoxides (14) were converted to the desired cyclic carbonates in yields up to 99 %. We could successfully recover and reuse the catalyst >20 times with excellent yields up to 99 %. Although, we observed that the activity gradually decreased after repetitive cycles. This decrease was attributed to KI leaching and partial degradation caused by mechanical stirring. This assumption is supported by scanning electron microscopy and energy dispersive X-ray spectroscopy.

Introduction

Global climate change is closely related to the rising level of anthropogenic greenhouse gases in the atmosphere;[1] the largest part is attributed to CO_2. Therefore, different strategies in managing CO_2 emissions are widely discussed.[2] In addition to reducing the output of CO_2, its utilization as a C1 building block is of considerable interest.[3] CO_2 is a readily abundant, cost-efficient, non-toxic carbon source. Thus, the utilization of CO_2 has the potential to lead to value added products.

The major challenge utilizing CO_2 in organic synthesis is its thermodynamic stability as well as kinetic inertia.[4] In chemical processes, usually high energy starting materials and/or conditions are required, such as epoxides and/or elevated temperatures. In this context the conversion of CO_2 with epoxides to the corresponding cyclic carbonates and polycarbonates are attractive reactions.[5] Cyclic carbonates are versatile products, which exhibit some outstanding properties, such as high boiling points, low toxicity, and odorless nature.[5c,6] They can be utilized as aprotic polar solvents, electrolytes in Li-ion batteries, and intermediates in polycarbonate and polyurethane synthesis.[7] Furthermore, the synthesis of cyclic carbonates from CO_2 and epoxides is an atom-economic reaction,[4,8] which is an important factor in sustainable development.[9] Thus, among all the reported CO_2 fixation routes, the synthesis of cyclic carbonates through the coupling of CO_2 with epoxides is one of the most attractive process and numerous catalytic systems for this reaction are reported.[3a,5d,10]

The utilization of readily available alkali metal salts as sustainable metal-based catalysts is of particular interest.[10a] However, owing to the low solubility in organic solvents and limited activity when used alone, they are generally combined with co-catalysts to overcome drawbacks. In this context KI is the most frequently employed salt. Early work by Kuran et al. established KI in combination with crown ethers as well as other phase-transfer agents as suitable catalyst systems for the conversion of CO_2 with epoxides.[11] Subsequently, studies on various co-catalysts were reported. This includes the utilization of polyethylene glycol as alternative to crown ethers.[12] Moreover, amine derivatives such as 4-dimethylaminopyridine,[13] polydopamine,[14] cucurbit[6]uril,[15] and triethanol amine[16] as well as simple hydroxyl group containing compounds for example, pentaerythritol,[17] propylene glycol,[18] and formic acid[19] were employed. Recently bio-based co-catalysts such as β-cyclodextrin,[20] cellulose,[21] lignin,[22] lecithine,[23] and even amino acids[24] attracted great attention. Usually KI is employed in catalyst loadings ranging from 0.1 up to 2.5 mol % with a wide range of co-catalyst concentration of up to 50 mol % or 66 wt %, respectively. The commonly reported CO_2 pressures in those procedures range between 20 and 60 bar with reaction temperatures of 100–130 °C. Even though, some of the reported catalyst systems[14–16,20] could be reused up to 7 times, one of the remaining challenges in this area is the development of efficient immobilized catalyst systems, which operate under mild conditions and might be suitable for implementation in continuous processes.[10a]

We reported bifunctional ammonium[25] and phosphonium[26] salts as efficient one-component catalysts for the conversion of CO_2 and epoxides. Subsequently, we developed highly active immobilized catalysts.[27] Recently, we also described KI in com-

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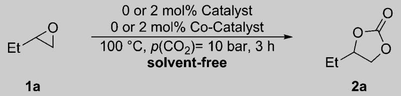
bination with amino alcohols and hydroxyl functionalized imidazoles to catalyze this reaction very efficiently even at temperatures $<100\,^{\circ}C$.[28] In our continuous efforts to develop effective and recyclable systems, we envisioned readily available and nonhazardous polydibenzo-18-crown-6 (poly18C6) to simultaneously serve two purposes in the combination with KI: Firstly as suitable co-catalyst and secondly as recyclable support.

Results and Discussion

We evaluated the feasibility of this concept in the conversion of 1,2-epoxybutane (**1 a**) with CO_2 to 1,2-butylene carbonate (**2 a**) under solvent-free conditions as a test reaction. Initially we performed the reaction at 100 °C, 10 bar CO_2 pressure (1 bar $=10^5$ Pa), 3 h reaction time, 2 mol% catalyst, if applicable, and equimolar amounts of poly18C6 as co-catalyst (Table 1). In the absence of a catalyst or co-catalyst no conversion of **1 a** was observed (entry 1). In the presence of 2 mol% KCl, KBr, or KI, no significant reaction was observed (entries 2–4). As expected, when poly18C6 was used alone, again no product formation was observed (entry 5). Next, we employed potassium halides as catalysts in combination with poly18C6 as co-catalysts (entries 6–8). In the case of KBr and KI, a significant increase in conversion was observed; the highest yield (89%) for **2 a** was obtained in the presence of KI (entries 7 and 8).

Table 1. Evaluation of different potassium halides as catalysts in combination with poly18C6 as co-catalyst.



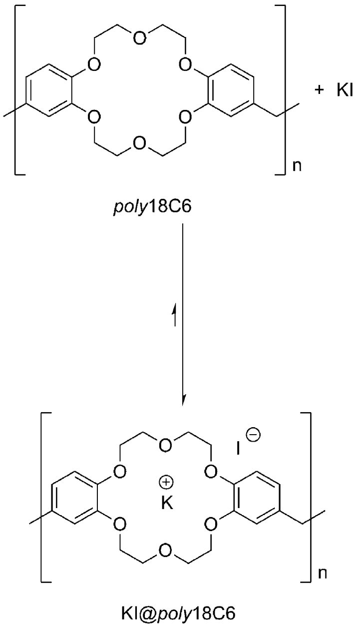
1a **2a**

Entry	Catalyst[a]	Co-catalyst[a]	Conv. **1 a**[b] [%]	Yield **2 a** [%][b]	TOF [h^{-1}]
1	–	–	0	0	–
2	KCl	–	0	0	–
3	KBr	–	0	0	–
4	KI	–	1	1	–
5	–	poly18C6	0	0	–
6	KCl	poly18C6	1	1	<1
7	KBr	poly18C6	56	56	9
8	KI	poly18C6	89	89	15
9	KI	18C6	67	67	11
10	KI	DB18C6	24	24	4

[a] 2 mol%. [b] Determined by GC-FID with *n*-hexadecane as internal standard.

The poor performance of the KCl and KBr in comparison to KI, as observed in our previous work[25,26,28] and also frequently reported in the literature, is commonly attributed to the increased ability of I^- to act as a leaving group.[10a,29] Additionally we utilized 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) as homogeneous co-catalysts in combination with KI (entries 9 and 10). Under the same reaction conditions the yield and activity were in both cases significantly lower compared to the poly18C6 system, indicating an additional synergistic effect from the support (entry 8 vs. entries 9–10).

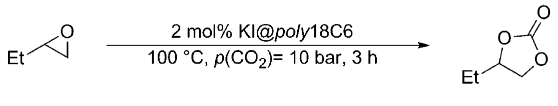
Further experiments were performed utilizing KI in combination with poly18C6 as most active system. As the in situ complexation of the cation by the crown ether seemed likely, we decided to load poly18C6 with KI prior to the reaction. The complexation of a metal cation by a crown ether is an equilibrium reaction;[30] hence, the polymeric crown ether poly18C6 was treated with a saturated solution of KI in methanol to shift the equilibrium towards the catalyst (KI) loaded poly18C6 (KI@poly18C6) (Scheme 1). The desired product was obtained after filtration. The KI loading was determined by elemental analysis and atom absorption spectroscopy to be 1.64 mmol $g_{polymer}^{-1}$.



Scheme 1. Synthesis of KI@poly18C6 by treating polydibenzo-18-crown-6 with KI in methanol. Reaction conditions: poly18C6, saturated solution of KI in methanol, $T=23\,^{\circ}C$, $t=2$ d.

Remarkably, the preloaded polymer KI@poly18C6 showed significantly higher activity compared to the in situ system (Scheme 2). Under the same reaction conditions, the test substrate **1 a** was converted with CO_2 in the presence of 2 mol% KI@poly18C6[31] to give **2 a** in 97% yield. Therefore, this catalyst was utilized for further optimization of the reaction parameters in the test reaction.

We previously observed that the catalyst amount and reaction temperature have by far the biggest impact on conversion and selectivity in this reaction. Thus, the influence of the reaction temperature was evaluated at $p(CO_2)=10$ bar and $t=3$ h (Figure 1). The yield of cyclic carbonate **2 a** improved with increasing temperature in the range of 50–120 °C. Notably, even at 50 °C the desired product **2 a** was obtained in 19% yield. Yet at 80 °C a reasonable yield of 74% of **2 a** was achieved. However, a temperature of 100 °C was necessary to obtain full conversion and 97% yield within 3 h.



1a **2a**, 97%

Scheme 2. Utilization of preloaded polymer KI@poly18C6 as the catalyst in the test reaction.

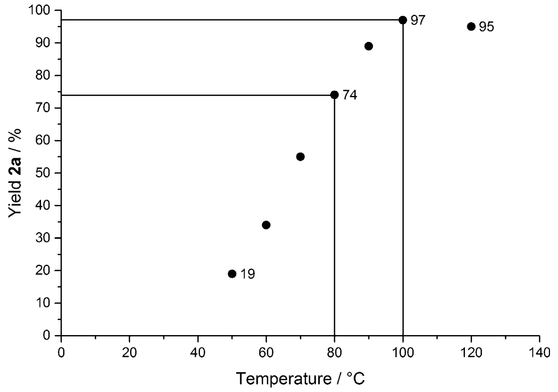


Figure 1. Temperature dependence of the test reaction. Reaction conditions: 25 mmol **1a**, $p(CO_2) = 10$ bar, $t = 3$ h, 2 mol% KI@poly18C6.

The product formation was examined with respect to the reaction time at 80 and 100 °C (Figure 2). At 100 °C, a reaction time of 0.5 h yielded over 50% of **2a**; however, a reaction time of 3 h was needed for full conversion and 97% yield. At 80 °C, **2a** was obtained in 74% yield after 3 h; however, full conversion of **1a** was achieved after a reaction time of 14 h and a yield of 99% of **2a**.

The influence of the CO_2 pressure was also evaluated. Therefore, the test reaction was performed applying various CO_2 pressures at 100 °C for 3 h with a catalyst concentration of 2 mol% (KI@poly18C6).[32] Pressures between 5 and 50 bar had no significant influence and yields $>90\%$ were obtained. Even at a low pressure (5 bar) a very good yield of 95% was obtained. Nevertheless, to promote the quantitative conversion of the substrate, a pressure of 10 bar was applied.

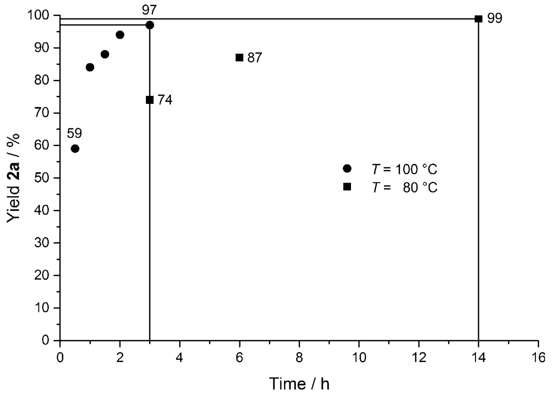
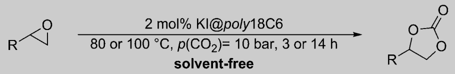


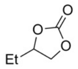
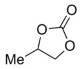
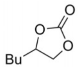
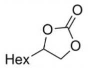
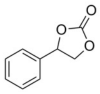
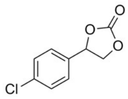
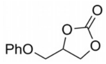
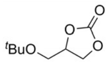
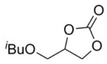
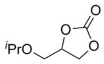
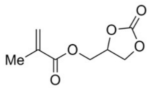
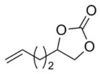
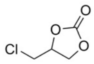
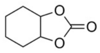
Figure 2. Time dependence of the test reaction. Reaction conditions: 25 mmol 1,2-epoxybutane (**1a**), $T = 100$ °C or 80 °C, $p(CO_2) = 10$ bar, 2 mol% KI@*poly*18C6.

Based on those results we explored the substrate scope (**1a**–**n**) for two different reaction conditions (80 °C, 14 h and 100 °C, 3 h) applying 10 bar CO_2 pressure and 2 mol% KI@poly18C6 (Table 2). All reactions were performed under solvent-free conditions and the desired products (**2a**–**n**) were obtained after filtration. In general, for both reaction conditions the products **2a**–**m** were isolated in excellent yields up to 99%. Notably, for aliphatic substrates **1a**–**d** at 100 °C and 3 h, a decrease in yield with increasing chain length of the alkyl substituents was observed. However, at 80 °C and 14 h reaction time excellent yields (93–97%) were achieved for **2a**–**d** (en-

Table 2. Substrate scope under optimized reaction conditions.[a]



1 **2**

Entry	Product		Isolated yield [%] Cond. 1[b]	Cond. 2[b]
1		**2a**	91	93
2		**2b**	92	93
3		**2c**	86	96
4		**2d**	81	97
5		**2e**	89	98
6		**2f**	83	99
7		**2g**	92	99
8 9		**2h**	91 80[c]	96
10		**2i**	93	93
11		**2j**	93	96
12		**2k**	91	98
13		**2l**	91	95
14		**2m**	90	98
15		**2n**	12	17

[a] Reaction conditions: 25 mmol **1**, 2 mol% KI@poly18C6, $p(CO_2) = 10$ bar. [b] Cond. 1: $T = 100$ °C, $t = 3$ h.; Cond. 2: $T = 80$ °C, $t = 14$ h. [c] $p(CO_2) = 1$ bar.

tries 1–4). Under the conditions of 100 °C and 3 h, aromatic substituted epoxides, such as styrene oxide (**1 e**) and 4-chlorostyrene oxide (**1 f**) were transformed into their respective carbonates **2 e** and **2 f** in yields of 89 and 83 %, respectively (entry 5 and 6). Again, higher yields of 98 % for **2 e** and 99 % for **2 f** were obtained at 80 °C and 14 h, respectively. Under both reaction conditions, glycidyl ethers (**1 g**–**j**) were converted into their corresponding cyclic carbonates **2 g**–**j** in yields >90 % (entries 7–11). At 100 °C, isolated yields of **2 g**–**j** up to 93 % were achieved. Interestingly, under more mild reaction conditions (80 °C and 14 h), higher yields of the carbonates **2 g**–**j** (93–99 %) were isolated. Notably, **2 h** could be obtained in 80 % yield even at 1 bar CO_2 pressure at 100 °C (entry 9). Unsaturated side chains were also tolerated as with epoxides **1 k**–**l** under these conditions, resulting in isolated yields of 91 % for **2 k**–**l** at 100 °C (entry 12 and 13). Again, under more mild conditions, the desired carbonates **2 k**–**l** were obtained in higher yields of 98 and 95 %, respectively. Moreover, epichlorohydrin (**1 m**) was converted at 100 °C and 80 °C to yield the desired product **2 m** in 90 and 98 % yield, respectively (entry 14).

Due to steric effects, internal epoxides, such as cyclohexene oxide (**1 n**), are generally challenging substrates for conversion with CO_2 to the corresponding carbonates.[25,26,33] Drastic reaction conditions for their conversion are often required. At 100 °C, carbonate **2 n** was isolated in 12 % yield after 3 h (entry 15), whereas utilizing KI@poly18C6 at 80 °C and 14 h a yield of 17 % of **2 n** was obtained.

The key advantage of KI@poly18C6 is the potential recyclability of this catalytic system, which can be easily separated from the reaction mixture either by filtration or product extraction. Thus, we thoroughly investigated the catalyst recycling. Our intention was to develop a recyclable system that efficiently converts epoxides **1** and CO_2 into cyclic carbonates **2** under mild reaction conditions ($T < 100$ °C). Therefore, we employed 2 mol % KI@poly18C6 in multiple consecutive runs of the test reaction at 80 °C and 10 bar CO_2. We drastically reduced the reaction time from 14 h to 6 h to study the catalyst efficiency and reveal potential loss of activity during the recycling process. The results of the recycling experiments are shown in Figure 3. Despite the reduction in reaction time, the obtained yield in the first two cycles was ≥95 %, which illustrates the high efficiency of the system even at low temperatures. However, the yield dropped from 99 % in the first run to 78 % in the sixth run and to 56 % in the tenth run. Elemental analysis of the isolated products revealed the presence of KI, which was attributed to catalyst leaching from the polymeric support. Catalyst leaching is a frequently observed problem for immobilized homogeneous catalysts.[34]

Regeneration of the catalyst was possible by treating the recovered polymer with a saturated solution of KI in methanol. The results for the first three runs utilizing the regenerated material indicate that the initial activity was successfully restored. The desired product **2 a** was obtained in yields of 97, 94, and 88 % in runs 11–13, respectively. Similar to before to regeneration, the yields dropped successively in the next seven runs, yet a yield of 43 % of **2 a** was still achieved in the 20th run (10th run after first regeneration). Notably, compared to 56 % in the 10th run, this yield was considerably lower. We decided to attempt to regenerate the catalyst material a second time and this again resulted in restored catalytic activity. In the 21st run (first run after second regeneration) a yield of 99 % of **2 a** was obtained. However, a dramatic loss in activity during the next two cycles was observed leading to a moderate yield of 60 % in the 23rd run.

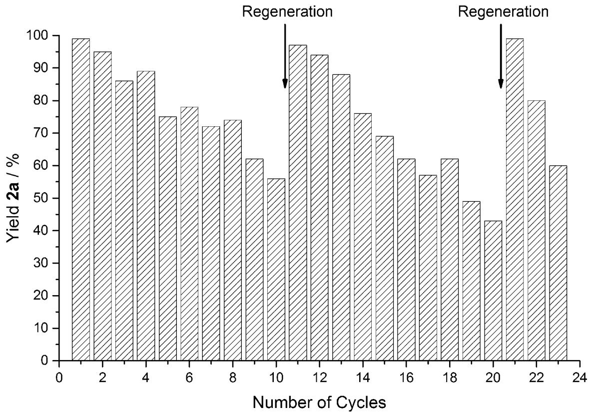


Figure 3. Recycling study of KI@poly18C6 in the test reaction. Reaction conditions: 2 mol % KI@poly18C6, $p(CO_2) = 10$ bar, $T = 80$ °C, $t = 6$ h. Yields were determined by ^{1}H NMR spectroscopy. The catalyst was regenerated after cycle 10 and cycle 20.

The loss of activity was attributed to leaching of KI as well as partial deterioration of the polymer resulting from thermal stress and mechanical stirring during the recycling experiments.[35] In general, the problem of catalyst leaching may be avoided by covalently binding the catalyst to a support.[27,36] However, depending on the reaction conditions and the support, partial decomposition might be observed, which could lead to a decrease in catalytic activity during the recycling process. Inorganic supports or salts are often more robust, but usually require drastic reaction conditions compared to the homogeneous systems.[37]

To investigate these assumptions on the loss of catalyst activity, we studied the catalyst material by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). These techniques were used to provide information about the morphological as well as elemental changes of the polymer supported catalyst upon loading with KI and after recycling. The SEM images of poly18C6 displayed particles of polymer with a clean surface (Figure 4 a). As expected, the corresponding EDX spectrum of poly18C6 (Figure 4 d) shows no significant signals for K (K-Kα at 3.314 keV) or I (I-Lα at 3.938 keV). Treating of poly18C6 with KI results in the loaded polymer
KI@poly18C6 with a KI loading of 1.64 mmol $g_{polymer}^{-1}$ as determined by elemental analysis. Accordingly, small particles are visible on the polymer surface using SEM, indicating impregnation with the metal halide (Figure 4 b). Indeed, the corresponding EDX spectrum from this area of the loaded polymer KI@poly18C6 showed signals for K at 3.314 keV and I at 3.938 keV (Figure 4 e), which further supports the effectiveness of KI loading. SEM experiments of the catalyst after run 10

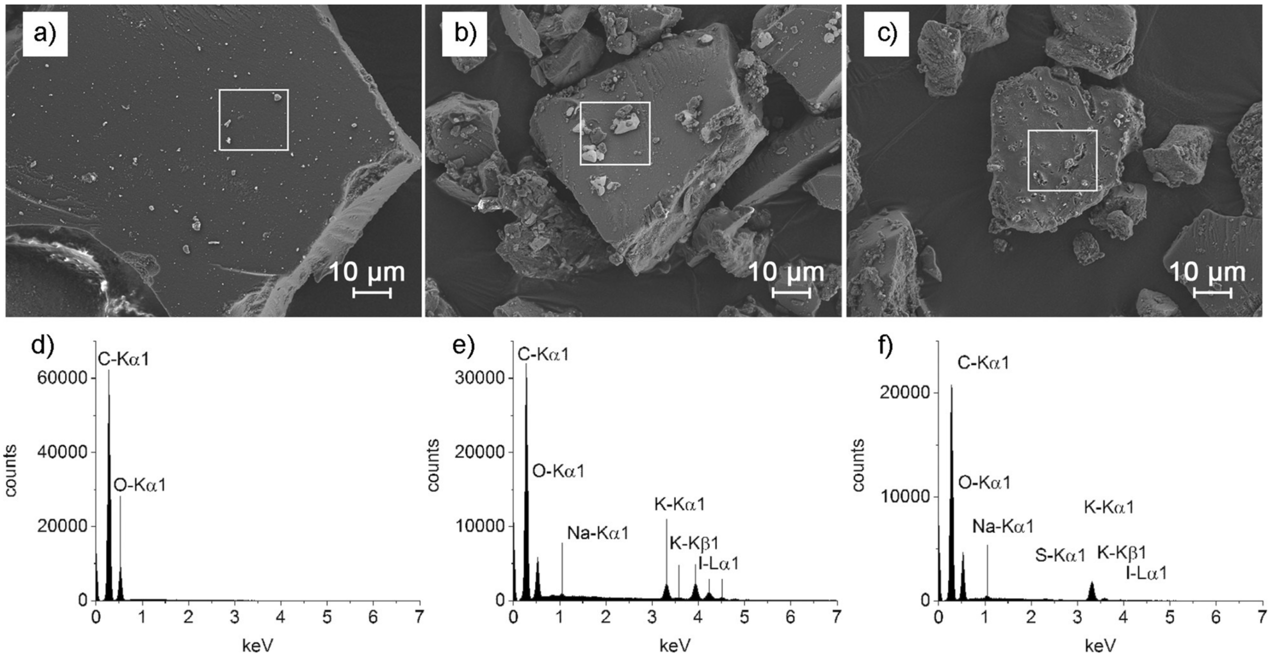


Figure 4. SEM images and EDX spectra of marked regions of (a, d) poly18C6, (b, e) KI@poly18C6, and (c, f) KI@poly18C6 after run 10, respectively.

showed significant morphological changes characterized by reduced overall particle size compared to KI@poly18C6 (Figure 4c). Additionally, a deterioration of the polymer surface was observed that manifested in cracks and cavities with few particles remaining. The EDX spectrum still indicates the presence of K at 3.314 keV, but the signal of the I-Lα at 3.938 keV was not observed, which suggests leaching of I^- from the catalyst after multiple runs (Figure 4f).

This view was supported by EDX elemental mappings performed for K and I to clarify the local distribution of these elements in the loaded polymer KI@poly18C6 prior to use and after 10 catalytic cycles (Figure 5). Interestingly, specific regions of high K and I concentration were observed for KI@poly18C6 (Figure 5a and c, respectively). Moreover, the distribution of both elements matched identically, which indicates the existence of KI particles in these regions. The EDX elemental maps for KI@poly18C6 after 10 catalytic cycles (Figure 5b and d) further illustrate the observations from the corresponding SEM image and EDX spectrum; while specific K-rich regions are still present on the catalyst surface, the absence of specific matching I-rich regions indicates leaching of I during the recycling procedure. Therefore, the reduced amount of I in the catalyst leads to the lower catalytic activity observed in the 10th run of the recycling experiments.

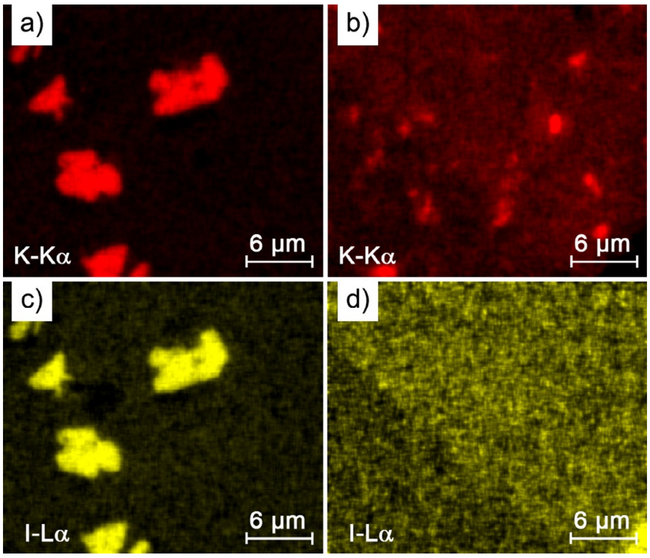


Figure 5. EDX element maps for K and I of (a, c) KI@poly18C6 and (b, d) KI@poly18C6 after run 10.

Conclusions

We report a highly active polymer-supported catalyst system for the conversion of epoxides with CO_2 under mild and solvent-free conditions. This system is based on the combination of KI with polydibenzo-18-crown-6 (poly18C6). Initially the combination of different potassium salts and poly18C6 were investigated. The in situ system consisting of poly18C6 and KI proved to be the most active one. However, the pretreatment of poly18C6 with KI yielded a polymer supported catalyst (KI@poly18C6) that showed even higher activity. Subsequently, two reaction protocols were determined and the substrate scope and limitation was evaluated. Thus, 14 epoxides were converted under solvent-free conditions at 100 °C, allowing for short reaction times. The desired cyclic carbonates were obtained in isolated yields up to 93 %. If the reaction was performed at 80 °C, yields up to 99 % were achieved after 14 h. We thoroughly evaluated the possibility of catalyst recycling and successfully recovered and reused the catalyst 23 times. Excellent to good yields were obtained in the first six cycles while a gradual decrease was observed thereafter. This loss in yield was attributed to KI leaching. Regeneration of the catalyst after the 10th and 20th run initially restored the activity. However, after the second regeneration a dramatic drop in yield was observed in the subsequent three runs. Accompanying SEM and EDX measurements revealed that leaching, as well as partial degradation caused by mechanical stirring, are the most likely reasons for the loss of activity. The atom-economic conversion of epoxides with CO_2 to cyclic carbonates has great potential as a key transformation for a sustainable society. The development of efficient recyclable systems remains a challenging goal. The results presented illustrate one possible option. However, more robust materials, which also prevent leaching from the support, are still desired.

Experimental Section

Preparation of KI@poly18C6

A large excess of KI in methanol (40 mL) was stirred for 12 h at 23 °C. The excess KI was filtered off and added to poly18C6 (3.66 g). This mixture was placed in a shaking device at 23 °C under air for 2 d. The loaded polymer was filtered off, washed with filtrate (2×2 mL), and dried under vacuum to yield KI@poly18C6 (5.97 g) as a brown powder. IR (ATR): $v = 3403$ (s), 2929 (m), 2872 (m), 1606 (s), 1508 (s), 1451(s), 1403 (m), 1257 (s), 1194 (vs), 1120 (vs), 1089 (vs), 1046 (vs), 951 (s), 912 (s), 747 cm^{-1} (s); elemental analysis found (%): K 6.40 (1.64 mmol g^{-1} loading).

Conversion of epoxides to cyclic carbonates

The autoclave (25 mL, stainless steel, Parr Instrument) was charged with KI@poly18C6 (0.02 equiv. KI based on KI-loading) and epoxide **1** (1.0 equiv.). The reactor was purged once with CO_2 and pressurized with CO_2 to 1.0 MPa. The reaction mixture was heated to 80 °C for 14 h (general procedure 1, GP1) or 100 °C for 3 h (general procedure 2, GP2), respectively. After completion the reactor was cooled with an ice bath and CO_2 was released slowly. The crude reaction mixture was extracted with dichloromethane and filtered through a silica plug. After removal of all volatiles under reduced pressure, cyclic carbonates **2** were obtained.

4-Ethyl-1,3-dioxolan-2-one (2a):[25,26b] According to GP1, 1,2-epoxybutane (**1a**, 1.80 g, 25.0 mmol) was converted with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup **2a** (2.70 g, 23.3 mmol, 93 %) was isolated as a colorless liquid. According to GP2, 1,2-epoxybutane (**1a**, 1.89 g, 26.2 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (270 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2a** (2.78 g, 23.9 mmol, 91 %) was isolated as a colorless liquid.^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.99$ (dt, $J = 7.5$, 2.1 Hz, 3 H), 1.67–1.82 (m, 2 H), 4.06 (dt, $J = 7.7$, 1.5 Hz, 1 H), 4.50 (dt, $J = 8.1$, 1.2 Hz, 1 H), 4.60–4.70 ppm (m, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 8.3$ (CH_3), 26.7 (CH_2), 68.9 (CH), 77.9 (CH), 155.0 ppm (C=O).

4-Methyl-1,3-dioxolan-2-one (2b):[25,26b] According to GP1, 1,2-epoxypropane (**1b**, 1.45 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2b** (2.37 g, 23.2 mmol, 93 %) was isolated as a colorless liquid. According to GP2, 1,2-epoxypropane (**1b**, 1.51 g, 26.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (253 mg, 1.98 mmol g^{-1} KI-loading). After workup the title compound **2b** (2.43 g, 23.8 mmol, 92 %) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.48$ (d, $J = 6.3$ Hz, 3 H), 4.02 (dd, $J = 8.4$, 7.2 Hz, 1 H), 4.55 (dd, $J = 8.4$, 7.7 Hz, 1 H), 4.80–4.91 ppm (m, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 19.4$ (CH_3), 70.6 (CH_2), 73.5 (CH), 155.0 ppm (C=O).

4-Butyl-1,3-dioxolan-2-one (2c):[25] According to GP1, 1,2-epoxyhexane (**1c**, 2.50 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2c** (3.47 g, 24.1 mmol, 96 %) was isolated as a colorless liquid. According to GP2, 1,2-epoxyhexane (**1c**, 2.55 g, 25.5 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (266 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2c** (3.14 g, 21.8 mmol, 86 %) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (t, $^3J = 6.9$ Hz, 3 H), 1.31–1.50 (m, 4 H), 1.64–1.83 (m, 2 H), 4.07 (dd, $J = 8.3$, 7.2 Hz, 1 H), 4.53 (dd, $J = 8.3$, 7.9 Hz, 1 H), 4.65–4.75 ppm (m, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 13.7$ (CH_3), 22.2 (CH_2), 26.3 (CH_2), 33.5 (CH_2), 69.3 (CH_2), 77.0 (CH), 155.0 ppm (C=O).

4-Hexyl-1,3-dioxolan-2-one (2d):[25,26b] According to GP1, 1,2-epoxyoctane (**1d**, 3.21 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2d** (4.17 g, 24.2 mmol, 97 %) was isolated as a colorless liquid. According to GP2, 1,2-epoxyoctane (**1d**, 3.25 g, 25.4 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (269 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2d** (3.55 g, 20.6 mmol, 81 %) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.8$ Hz, 3 H), 1.28–1.49 (m, 8 H), 1.61–1.83 (m, 2 H), 4.06 (dd, $J = 8.3$, 7.2 Hz, 1 H), 4.52 (dd, $J = 8.3$, 7.9 Hz, 1 H), 4.65–4.75 ppm (m, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 13.9$ (CH_3), 22.4 (CH_2), 24.2 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 33.8 (CH_2), 69.3 (CH_2), 77.0 (CH), 155.0 ppm (C=O).

4-Phenyl-1,3-dioxolan-2-one (2e):[25,26b] According to GP1, styrene oxide (**1e**, 3.00 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (271 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2e** (4.03 g, 24.5 mmol, 98 %) was isolated as a colorless solid. According to GP2, styrene oxide (**1e**, 3.16 g, 26.3 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (271 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2e** (3.86 g, 23.5 mmol, 89 %) was isolated as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.35$ (dd, $J = 8.6$, 7.9 Hz, 1 H), 4.80 (dd, $J = 8.6$, 8.2 Hz, 1 H), 5.68 (t, $J = 8.0$ Hz, 1 H), 7.34–7.48 ppm (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 77.1$ (CH_2), 77.9 (CH), 125.8 (CH), 129.2 (2×CH), 129.7 (2×CH), 135.7 (C), 154.8 ppm (C=O).

4-(4-Chlorophenyl)-1,3-dioxolan-2-one (2f):[25] According to GP1, 2-(4-chlorophenyl)oxirane (**1f**, 2.57 g, 16.6 mmol) was allowed to react with CO_2 in the presence of catalytic amounts of KI@poly18C6 (168 mg, 1.98 mmol g^{-1} KI-loading). After workup the title compound **2f** (3.26 g, 16.4 mmol, 99 %) was isolated as a colorless solid. According to GP2, 2-(4-chlorophenyl)oxirane (**1f**, 3.90 g, 25.2 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (268 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2f** (4.15 g, 20.9 mmol, 83 %) was isolated as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.30$ (dd, $J = 8.6$, 7.9 Hz, 1 H), 4.80 (t, $J = 8.4$ Hz, 1 H), 5.66 (t, $J = 8.0$ Hz, 1 H), 7.28–7.33 (m, 2 H), 7.40–7.44 ppm (m, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 71.0$ (CH), 76.6 (CH), 127.2 (2×CH), 129.5 (2×CH), 134.2 (C), 135.7 (C), 154.5 ppm (C=O).

4-(Phenoxymethyl)-1,3-dioxolan-2-one (2g):[25,26b] According to GP1, phenyl glycidyl ether (**1g**, 3.75 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2g** (4.79 g, 24.7 mmol, 99%) was isolated as a colorless solid. According to GP2, phenyl glycidyl ether (**1g**, 3.80 g, 25.3 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (253 mg, 1.98 mmol g^{-1} KI-loading). After workup the title compound **2g** (4.52 g, 23.3 mmol, 92%) was isolated as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=4.14$ (dd, $J=10.6$, 3.6 Hz, 1H), 4.25 (dd, $J=10.6$ Hz, 4.1 Hz, 1H), 4.54 (dd, $J=8.5$, 6.0 Hz, 1H), 4.62 (t, $J=8.4$ Hz 1H), 5.00–5.07 (m, 1H), 6.89–6.94 (m, 2H), 7.00–7.05 (m, 1H), 7.27–7.35 ppm (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=66.2$ (CH_2), 66.8 (CH_2), 74.1 (CH), 114.5 (CH), 121.9 (2×CH), 129.6 (2×CH), 154.7 (C=O), 157.7 ppm (C).

4-(Tert-butoxymethyl)-1,3-dioxolan-2-one (2h):[25] According to GP1, tert-butyl glycidyl ether (**1h**, 3.25 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2h** (4.19 g, 24.1 mmol, 96%) was isolated as a colorless liquid. According to GP2, tert-butyl glycidyl ether (**1h**, 3.27 g, 25.1 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (269 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2h** (3.81 g, 21.9 mmol, 87%) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.18$ (s, 9H), 3.51 (dd, $J=10.4$, 3.6 Hz, 1H), 3.61 (dd, $J=10.4$, 4.4 Hz, 1H), 4.37 (dd, $J=8.3$, 5.9 Hz, 1H), 4.46 (t, $J=8.2$ Hz, 1H), 4.73–4.80 ppm (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=27.2$ (3×CH_3), 61.2 (CH_2), 66.4 (CH_2), 73.7 (C), 75.2 (CH), 155.1 ppm (C=O).

4-(Iso-butoxymethyl)-1,3-dioxolan-2-one (2i):[25] According to GP1, iso-butyl glycidyl ether (**1i**, 3.27 g, 25.1 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2i** (4.05 g, 23.2 mmol, 92%) was isolated as a colorless liquid. According to GP2, iso-butyl glycidyl ether (**1i**, 3.24 g, 24.9 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (253 mg, 1.98 mmol g^{-1} KI-loading). After workup the title compound **2i** (4.01 g, 23.0 mmol, 93%) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.89$ (d, $J=6.7$ Hz, 6H), 1.85 (sept, $J=6.7$ Hz, 1H), 3.26 (d, $J=6.6$ Hz, 2H), 3.59 (dd, $J=11.0$, 3.5 Hz, 1H), 3.67 (dd, $J=11.0$, 3.8 Hz, 1H), 4.40 (dd, $J=8.3$, 6.0 Hz, 1H), 4.49 (t, $J=8.3$ Hz, 1H), 4.77–4.84 ppm (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=19.0$ (2×CH_3), 28.3 (CH), 66.2 (CH_2), 69.7 (CH_2), 75.1 (CH), 78.7 (CH_2), 155.0 ppm (C=O).

4-(Iso-propoxymethyl)-1,3-dioxolan-2-one (2j):[25,26b] According to GP1, iso-propyl glycidyl ether (**1j**, 2.81 g, 24.2 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (295 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2j** (3.70 g, 23.1 mmol, 96%) was isolated as a colorless liquid. According to GP2, iso-propyl glycidyl ether (**1j**, 2.89 g, 24.9 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (252 mg, 1.98 mmol g^{-1} KI-loading). After workup the title compound **2j** (3.71 g, 23.2 mmol, 93%) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.15$ (d, $J=6.0$ Hz 6H), 3.56–3.68 (m, 3H), 4.37 (dd, $J=8.3$, 6.0 Hz, 1H), 4.49 (t, $J=8.3$ Hz, 1H), 4.75–4.82 ppm (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=21.7$ (CH_3), 21.8 (CH_3), 66.4 (CH_2), 67.0 (CH_2), 72.9 (CH), 75.1 (CH), 155.0 ppm (C=O).

(2-Oxo-1,3-dioxolan-4-yl)methyl methacrylate (2k):[25,26b] According to GP1, glycidyl methacrylate (**1k**, 3.55 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2k** (4.57 g, 24.5 mmol, 98%) was isolated as a colorless liquid. According to GP2, glycidyl methacrylate (**1k**, 3.62 g, 25.5 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (266 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2k** (4.34 g, 23.3 mmol, 91%) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.94$ (t, $J=1.2$ Hz, 3H), 4.29–4.36 (m, 2H), 4.42 (dd, $J=12.6$, 3.1 Hz, 1H), 4.58 (dd, $J=8.6$, 8.5 Hz, 1H), 4.94–5.00 (m, 1H), 5.64 (pent, $J=1.5$ Hz, 1H), 6.13–6.15 ppm (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=18.1$ (CH_3), 63.4 (CH_2), 66.0 (CH_2), 73.8 (CH), 127.2 (CH_2), 135.1 (CH), 154.4 (C=O), 166.6 ppm (C=O).

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (2l):[25,26b] According to GP1, 1,2-epoxy-5-hexene (**1l**, 2.44 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (253 mg, 1.98 mmol g^{-1} KI-loading). After workup the title compound **2l** (3.37 g, 23.7 mmol, 95%) was isolated as a colorless liquid. According to GP2, 1,2-epoxy-5-hexene (**1l**, 2.47 g, 25.2 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (268 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2l** (3.27 g, 23.0 mmol, 91%) was isolated as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.71$–1.86 (m, 1H), 1.88–1.98 (m, 1H), 2.11–2.30 (m, 2H), 4.08 (dd, $J=8.4$, 7.20 Hz, 1H), 4.53 (dd, $^3J=8.4$, 7.9 Hz, 1H), 4.68–4.77 (m, 1H), 5.02–5.11 (m, 2H), 5.71–5.85 ppm (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=28.6$ (CH_2), 32.9 (CH_2), 69.2 (CH_2), 76.3 (CH), 116.3 (CH_2), 136.0 (CH), 154.9 ppm (C=O).

4-(Chloromethyl)-1,3-dioxolan-2-one (2m):[25,26b] According to GP1, epichlorohydrin (**1m**, 2.31 g, 25.3 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (305 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2m** (3.23 g, 23.6 mmol, 90%) was isolated as a colorless liquid. According to GP2, epichlorohydrin (**1m**, 2.44 g, 26.4 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (266 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2m** (3.23 g, 23.6 mmol, 90%) was isolated as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.72$ (dd, $J=12.2$, 3.7 Hz, 1H), 3.80 (dd, $J=12.2$, 5.2 Hz, 1H), 4.39 (dd, $J=8.8$, 5.7 Hz, 1H), 4.58 (dd, $J=8.8$, 8.4 Hz, 1H), 4.95–5.00 ppm (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta=43.8$ (CH_2), 66.9 (CH_2), 74.3 (CH), 154.2 ppm (C=O).

Cyclohexene carbonate (2n):[25,26b] According to GP1, cyclochexene oxide (**1n**, 2.45 g, 25.0 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (306 mg, 1.64 mmol g^{-1} KI-loading). After workup the title compound **2n** (589 mg, 4.15 mmol, 17%) was isolated as a colorless solid. According to GP2, cyclochexene oxide (**1n**, 2.48 g, 25.3 mmol) was allowed to react with CO_2 in the presence of KI@poly18C6 (268 mg, 1.16 mmol g^{-1} KI-loading). After workup the title compound **2n** (429 mg, 3.02 mmol, 12%) was isolated as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.36$–1.47 (m, 2H), 1.57–1.69 (m, 2H), 1.87–1.92 (m, 4H), 4.65–4.72 ppm (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta=19.1$ (2×CH_2), 26.7 (2×CH_2), 75.7 (2×CH), 155.3 ppm (C=O).

Recycling of KI@poly18C6

The autoclave was charged with KI@poly18C6 (610 mg, 1.64 mmol g^{-1} KI-loading, 0.02 equiv.), and 1,2-epoxybutane (**1a**, 3.60 g, 50.0 mmol, 1.0 equiv.). The reactor was purged once with CO_2 and pressurized with CO_2 to 1.0 MPa. The reaction mixture was heated to 80 °C for 6 h. Conversion, selectivity, and yield were determined by ^{1}H NMR spectroscopy of an aliquot of the crude reaction mixture. Subsequently the reaction mixture was extracted with cyclohexane/ethyl acetate ($v/v=10:3$, 3×26 mL). The organic layers were combined and all volatiles were removed under vacuum to yield cyclic carbonate **2a**. After run 10 and 20 the isolated catalyst was regenerated according to the KI@poly18C6 preparation procedure above.

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[31] Please Note: The amount of catalyst in mol % refers to the molar amount of potassium iodide.

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