Adding Value to Power Station Captured CO\(_2\): Tolerant Zn and Mg Homogeneous Catalysts for Polycarbonate Polyol Production

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ABSTRACT: Using captured waste carbon dioxide (CCU) as a chemical reagent is an attractive means to add value to carbon capture and storage (CCS) and is a high-priority target for manufacturing. One promising route is to copolymerize carbon dioxide and epoxides, to prepare aliphatic polycarbonates. In this study, three homogeneous dinuclear Zn and Mg catalysts, previously reported by our group (see Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. Angew. Chem., Int. Ed. 2009, 48, 931–933 and Kember, M. R.; Williams, C. K. J. Am. Chem. Soc. 2012, 134, 15676–15679) have been investigated using captured and contaminated carbon dioxide, with cyclohexene oxide, to produce polymers. Carbon dioxide captured from the carbon capture demonstrator plant at Ferrybridge Power Station, U.K., is applied for the efficient production of poly(cyclohexylene carbonate). Remarkably, the dinuclear Zn and Mg catalysts display nearly equivalent turnover numbers (TON) and turnover frequencies (TOF) using captured CO\(_2\) versus those using purified CO\(_2\). The tolerance of the catalysts to reactions contaminated with known quantities of exogenous water, nitrogen, SO\(_2\), amine, and octadecanethiol are reported. The catalyst activities, productivities, and selectivities are presented, together with the polymers’ number-average molecular weights (M\(_n\)), dispersities (D), and end-group analyses. The catalysts show high tolerance to protic impurities, including the addition of amine, thiol, and water. In particular, under certain conditions, efficient polymerization can be conducted in the presence of up to 400 equiv of water without compromising catalytic activity/productivity or selectivity. Furthermore, the catalysts can selectively produce polycarbonate polyols with molecular weights in the range of 600–9000 g/mol and dispersities <1.10.

KEYWORDS: carbon dioxide, copolymerization, polymerization, catalysis, homogeneous catalyst, zinc catalyst, magnesium catalyst, carbon capture and utilization, polycarbonate, controlled polymerization, carbon dioxide capture

INTRODUCTION

Using waste CO\(_2\) as a renewable raw material for the production of chemicals and materials is a particularly desirable means to add value to carbon capture and storage (CCS) and by analogy is frequently termed carbon dioxide capture and utilization (CCU). Although CCU could be highly attractive from both an economic and environmental perspective, there are only a few practical examples of its implementation. One successful commercial process is the pilot-scale production of methanol, demonstrated by Carbon Recycling International, which applies waste CO\(_2\) and H\(_2\) produced by water electrolysis using renewable power. Another example is the application of purified CO\(_2\), captured from power generation, termed the “Dream” process and realized by Bayer for the production of poly(ether carbonates). In the context of CCU, the metal-catalyzed copolymerization of CO\(_2\) with epoxides is interesting because of the high uptake of CO\(_2\) into the product. In an industry where raw material costs routinely account for >90% of production market prices, the substitution of costly petrochemical feedstocks with a low-cost feedstock such as CO\(_2\) is an exciting prospect. Indeed, materials which are 30–50 mol % derived from CO\(_2\) can be easily produced. The product aliphatic polycarbonates are proposed as petrochemical substitutes in applications such as films, packaging, and rigid plastics. Of particular interest are applications of low molecular-weight polycarbonate polyols as viable alternatives to the petrochemical polyols commonly applied in the manufacture of polyurethanes. The commercialization of polycarbonate polyols, derived from CO\(_2\), is an area of intense activity and pilot scale production is already underway. Central to the viability of the copolymerization process is the selection of the catalyst; both homogeneous and heterogeneous catalysts are known. While heterogeneous catalysts are being commercialized, they can suffer from low rates, require high pressures of purified carbon dioxide, and result in rather low uptakes of CO\(_2\), yielding poly(ether carbonates). Thus, if high CO\(_2\) uptake and concomitant formation of polycarbonates is desired, then homogeneous catalysts may be preferable.

Currently, a rather limited range of homogeneous catalysts suitable for this catalysis have been described, most of which have been included in recent reviews. Of these, significant
attention has focused on Co-salen complexes and their derivatives. The most effective of these have salen ligands incorporating ionic co-catalysts, commonly alkyl ammonium salts. There have been several interesting reports of strategies to recycle and reuse these catalysts from polymerization reactors. Although these catalysts exhibit high activities and selectivities, they also generally require higher CO2 pressures and typically apply the highest purity epoxides, which are subsequently reacted under rigorously anaerobic and anhydrous conditions. We have previously reported a series of homogeneous binuclear catalysts, comprising coordination complexes of macrocyclic ligands with dinuclear Zn(II), Co(II/III), Fe(III), and Mg(II) metal centers. In particular, the colorless, air-stable, low-cost, dinuclear Zn or Mg catalysts showed highly competitive activities and selectivities even in the presence of an excess of water (up to 30 mol equiv vs catalyst). Additionally, these catalysts performed equivalently to some Co-salen complexes even at very low pressures of CO2 (ca. 1−5 bar). A full kinetic study (N2 catalysts) revealed a zero-order dependence on CO2 pressure, over the range 1−40 bar. These promising characteristics prompted the current investigation into the tolerance of such dinuclear catalysts to a range of impurities found in captured CO2. To the best of our knowledge, such studies are critical to successful CCU implementation yet have not been routinely investigated/published. A notable exception is a recent relevant study by Darensbourg and co-workers, where metal-organic frameworks were used to store pure CO2 and then release it for subsequent copolymerization studies. It should, however, be noted that the parallels between the catalysts for cyclic carbonate and polymerization are limited: cyclic carbonates are the thermodynamic products and as such are generally favored over polymers using most catalysts. Furthermore, polymerization catalysts are usually designed as “leave in” and thus recycling strategies are different.

Herein, the previously reported homogeneous dinuclear Zn/Mg catalysts are applied to the production of poly(cyclohexene carbonate), using contaminated waste CO2. The polymerizations are conducted under 1 bar pressure of CO2, as model conditions for a desirable CCU process. Furthermore, the polymerizations have been conducted using concentrations of common poisons and contaminants higher than those commonly encountered in captured CO2 to demonstrate the extent of the robustness of these systems.

### RESULTS AND DISCUSSION

CCU relies on recycling waste CO2 streams as chemical feedstocks; in this context, CO2 streams produced by power generation are some of the most contaminated. Therefore, in order to investigate the tolerance of the catalysis, such contaminated gases were targeted.

It is clear that carbon dioxide captured from any industrial source (power plant or other) will contain impurities and the most common of these include water, nitrogen, oxygen, and, if
Table 2. Performance of 3 in the Presence of Different Gas-Phase Additives

| entry | additive | concn./vol. % | TON | TOF/h | selectivity | $M_{\text{n}}$ g/mol (D) |
|-------|----------|---------------|-----|-------|-------------|--------------------------|
| A     | none     |               | 477 | 159   | 99          | 6300 (1.04), 2800 (1.09) |
| B     | none     |               | 305 | 101   | 99          | 5900 (1.03), 2700 (1.09) |
| C     | H$_2$O   | 0.68          | 437 | 146   | 99          | 8300 (1.03), 4300 (1.09) |
| D     | N$_2$    | 5             | 439 | 146   | 99          | 7300 (1.04), 3100 (1.12) |
| E     | N$_2$    | 50            | 96  | 32    | 97          | ~600 ($\sim$1.2) |
| F     | N$_2$    | 75            | 88  | 29    | 95          | ~600 ($\sim$1.2) |
| G     | CH$_4$   | 5             | 447 | 149   | 99          | 7500 (1.05), 3200 (1.11) |
| H     | O$_2$    | 5             | 458 | 153   | 99          | 9000 (1.04), 4000 (1.09) |
| I     | H$_2$S   | 5             | 515 | 172   | 99          | 3000 (1.39) |
| J     | SO$_2$   | 0.05          | 383 | 127   | 99          | 4600 (1.03), 2100 (1.09) |

- Reaction conditions: 0.1 mol % of 3, 5 mL of CHO, 3 h reaction time, 1.06 bar of CO$_2$.  
- Pre-mixed into gas feed.  
- Selectivity for polycarbonate vs cyclic carbonate, determined by $^1$H NMR spectroscopy.  
- Only approximate values are given, since part of this mass range is outside the calibrated weight range of SEC experiments.
Upon dilution of the CO2 feed by 50%, a non-linear decrease in H2O and CO2 were pre-mixed in a 2 L reactor held at 150 °C cylinder. To simulate a truly "supplied by a balloon rather than a regulated supply from a cylinder." This case are likely due to the significantly lower overpressure supplied by a balloon rather than a regulated supply from a cylinder. As would be expected, higher catalyst loadings afforded a higher degree of monomer conversion, at fixed reaction times, and consequently higher molecular weight polymers. The dispersions were low in all cases and are consistent with well-controlled polymerizations as reported previously.21

To further demonstrate the practical utility of 3 in any CCU scenario, its tolerance to other CO2 sources and to high levels of various model contaminants was investigated (Tables 3 and 4). Importantly, it was found that commercial "food-grade" CO2 also resulted in activities and molecular weight distributions very similar to those in the aforementioned runs using captured CO2 (Table 3, entry B).20 The lower rates in this case are likely due to the significantly lower overpressure supplied by a balloon rather than a regulated supply from a cylinder. To simulate a truly "wet" feed, known volumes of H2O and CO2 were pre-mixed in a 2 L reactor held at 150 °C (ca. 0.6 bar overpressure), theoretically simulating 0.63 wt % H2O contamination (Table 3, entry C). Once again, the catalysis proceeds at a very similar rate, producing polymers with extremely similar molecular weights, in comparison to using purified CO2 supplied at the same overpressure (Table 3, entry A). Although it is difficult to ascertain and generalize the nature of the contaminants found in reclaimed CO2, both reduced and oxidized compounds of nitrogen (N2, amines, NO and NO) and sulfur (H2S, SO2 and SO3), O2 and H2O are common contaminants, and are not in the range targeted for polyols for polyurethane manufacture. As with H2S, the SEC analysis reveals a significant reduction in molecular weight, suggesting that H2S may be acting as a CTA under these conditions (supported by solution-phase experiments using H2S; see Figure S1 in the Supporting Information). While no detectable loss in selectivity was apparent by 1H NMR spectroscopy, the MALDI-TOF MS using a thiol chain transfer agent does show the presence of polymer series in which one or two ether linkages are present (Figure S1). In addition to reduced sulfur contaminants, post-combustion feeds are often contaminated by oxidized sulfurous impurities, namely SO2 and SO3, albeit at very low concentrations (Table 1).22 When the polymerization was carried out using a pre-mixed CO2 feed containing 500 ppm of SO2, there was a modest but reproducible reduction in TOF (Table 3, entry J). It is not clear if this reduction is due to a dilution and/or competitive inhibition effect, due to the greater solubility of SO2 relative to CO2, or to chemical reactivity.23 For example, the insertion of SO2 into Zn−alkyl bonds has been used to generate active catalysts for CHO/CO2 copolymerization from alkylzinc complexes.24 It could be envisaged that SO2 might compete with CO2 in the reversible insertion into the proposed propagating alkoxide bonds (Mg−OR). In any case, the concentration of SO2 used corresponds to ca. 70 times the expected contamination level (Table 1) and thus it is not envisaged that "normal" levels of this contaminant would have a significant effect on the rate.

Having assessed the robustness of 3 to the presence of some common gas-phase contaminants pre-mixed into the gas feed, it was also prudent to investigate its tolerance to some other potential homogeneous contaminants present (Table 4). Using unpurified CHO resulted in a modest rate enhancement in comparison to distilled samples (Table 4, entry A; Figure S2, Supporting Information). Various types of amine-based solvents are commonly proposed for CO2 capture technologies.25 For this study, diethylamine and monoethanolamine (H2N(CH2)2OH, MEA) were selected as practical model contaminants. When polymerizations were conducted using diethylamine, even at unrealistically high relative loadings (20 molar equiv based on 3 to investigate a "worst case" scenario; Table 4, entry B), the activity of 3 is marginally increased relative to the control (entry A, Table 3). As with H2S, the unimodal molecular weight distribution and substantial decrease in Mn are indicative of chain transfer and the much lower monomer conversions.21 Curiously, a modest but consistent rate enhancement was observed when H2S was present in the feed (Table 3, entry I). Although the origin of this enhancement in rate is not clear, analysis of the SEC data reveals a significant reduction in molecular weight, suggesting that H2S may be acting as a CTA under these conditions (supported by solution-phase experiments using H2S; see Figure S1 in the Supporting Information). While no detectable loss in selectivity was apparent by 1H NMR spectroscopy, the MALDI-TOF MS using a thiol chain transfer agent does show the presence of polymer series in which one or two ether linkages are present (Figure S1). In addition to reduced sulfur contaminants, post-combustion feeds are often contaminated by oxidized sulfurous impurities, namely SO2 and SO3, albeit at very low concentrations (Table 1).22 When the polymerization was carried out using a pre-mixed CO2 feed containing 500 ppm of SO2, there was a modest but reproducible reduction in TOF (Table 3, entry J). It is not clear if this reduction is due to a dilution and/or competitive inhibition effect, due to the greater solubility of SO2 relative to CO2, or to chemical reactivity.23 For example, the insertion of SO2 into Zn−alkyl bonds has been used to generate active catalysts for CHO/CO2 copolymerization from alkylzinc complexes.24 It could be envisaged that SO2 might compete with CO2 in the reversible insertion into the proposed propagating alkoxide bonds (Mg−OR). In any case, the concentration of SO2 used corresponds to ca. 70 times the expected contamination level (Table 1) and thus it is not envisaged that "normal" levels of this contaminant would have a significant effect on the rate.

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| entry | additive | amount | TON | TOF/h | selectivity | Mn (g/mol) |
|-------|----------|--------|-----|-------|-------------|------------|
| A     | none     | 20     | 511 | 176   | 99          | 2900 (1.45)|
| B     | HNEt     | 20     | 487 | 162   | 99          | 1200 (1.14)|
| C     | MEA      | 20     | 306 | 102   | 99          | 1300 (1.18)|
| D     | HSC(CH3) | 20     | 521 | 173   | 99          | 1600 (1.13)|
| E     | H2O      | 39     | 294 | 98    | 99          | ~600 (1.2) |
| F     | H2O      | 68     | 200 | 67    | 99          | oligomers  |
| G     | H2O      | 109    | 120 | 40    | 99          | oligomers  |

"Reaction conditions: 0.1 mol % of 3, 5 mL of CHO, 3 h reaction time, 1.06 bar of CO2. a Weighed directly into reaction vessel. b Based on 3. c TON = (mol of epoxide consumed)/(mol of catalyst). d Selectivity for polycarbonate vs cyclic carbonate, determined by 1H NMR spectroscopy, and comparison of the relative integrals of the lowest field resonances of polycyclohexene carbonate at 4.65 ppm and cyclohexene carbonate at 4.05 ppm. No ether linkages were detected. e Determined by SEC using narrow molecular weight polystyrene standard as the calibrants. f Unpurified CHO from Acros Organics, 98% (GC)."
1H NMR and MALDI-TOF MS spectra of the polymer produced in the presence of diethylamine clearly reveal −NEt2 terminated polymers (Figures S3 and S4, Supporting Information). High loadings of MEA are tolerated less well by 3 (Table 3, entry C), giving a substantial drop in rate (ca. 30%) along with a reduction in $M_n$ that is anticipated, given the presence of both primary hydroxyl and primary amino functionalities in MEA (see MALDI-TOF mass spectrum in Figure S5, Supporting Information). It is again worth drawing attention to the fact that high levels of MEA used in this experiment were chosen to represent an upper-end extreme scenario and are not anticipated to reach these levels in any real CCS process. To corroborate the previously determined rate enhancement in the presence of H2S, HSC18H37 was selected as an easily handled solution-phase analogue for comparison. A consistent increase in TOF and reduction of $M_n$ were again observed (Table 4, entry D). The presence of −SC18H37 end groups is easily identified in the MALDI-TOF MS spectra of the polymer and confirms the notion that it is acting as a CTA (Figure S6, Supporting Information). The propensity for thiols to function as chain transfer agents can be rationalized by the higher acidity of H2S ($pK_a = 7$) in comparison to H2O ($pK_a = 15$).26 Taken together, it appears that the inclusion of small amounts of non-aqueous CTAs (such as amines, thiols, and the impurities present in unpurified CHO) actually give marginal increases in TOF.

The preceding experiments employing waste CO2 (Table 2) and CO2 contaminated with water (Table 3, entry C) as well as the previously published studies using carbon dioxide mixed with added H2O have all demonstrated tolerance of 3 to H2O and other contaminants in captured gas streams. It is, however, of interest to further examine the specific effect of added water, as this would be expected to be a common contaminant of both epoxides and carbon dioxide. It is clear that adding a large excess of water (>40 molar equiv vs 3) exerts a negative effect on the relative activity of 3 (Figure 2) and reduces the $M_n$ of the material produced (Table 4, entries E–G). The origin of the loss in activity is not clear but may result from competitive binding of water.27 On the other hand, it does yield exclusively the dihydroxyl-terminated polymer (polyol) (Figure 2). This improvement in end-group selectivity is due to the ability of water to act as a chain transfer agent or to generate cyclohexenediol and to produce telechelic polymers. A major

### Table 5. Polymerizations using 3 Conducted in a Mechanically Stirred Reactor

| entry | amt of 3/mol % | p(CO2)/bar | t/h | T/°C | amt of H2O/ equiv | TON | TOF selectivity$^d/%$ | carbonate linkages$^d/%$ | $M_n$ g/mol$^e$ | $Đ$ |
|-------|----------------|-------------|-----|------|------------------|-----|----------------------|------------------------|----------------|-----|
| A     | 0.02           | 10          | 6   | 90   | 48               | 2300| 400                  | 99                     | 99             | 5000 | 1.09|
| B     | 0.01           | 10          | 2   | 125  | 48               | 6700| 3350                 | 99                     | 99             | 54900| 1.22|
| C     | 0.01           | 40          | 2   | 125  | 48               | 5900| 2950                 | 99                     | 99             | 43000| 1.20|
| D     | 0.003          | 10          | 5   | 125  | 192              | 2690| 5400                 | 99                     | 99             | 7200 | 1.06|
| E     | 0.003          | 10          | 4   | 125  | 400              | 9200| 2300                 | 99                     | 99             | 2300 | 1.08|

$^a$Reaction conditions: see the Experimental Section. $^b$Based on 3. $^c$TON = (mol of epoxide consumed)/(mol of catalyst). $^d$Selectivity for polycarbonate vs cyclic carbonate, determined by 1H NMR spectroscopy, and comparison of the relative integrals of the lowest field resonances of poly(cyclohexene carbonate) at 4.65 ppm and cyclohexene carbonate at 4.05 ppm. No ether linkages were detected (see carbonate linkages column). $^e$Determined by SEC using narrow molecular weight polystyrene standards as the calibrants.
application for these polymers is as polycarbonate polyols; thus, the production of dihydroxyl-terminated polymers is important.

Thus, these studies clearly reveal the promise for this class of homogeneous polymerization catalysts using captured or impure carbon dioxide gas streams. Although it is extremely difficult to unambiguously explain why these catalysts show such superior stabilities, factors such as catalyst structure and resting state are likely to be implicated. The high catalyst tolerance, particularly to protic impurities, relates to the catalyst structures where the chelate rings of the macrocycles and O,N donors stabilize the metals to ligand dissociation. Another factor is the stability of the initiating groups; the co-ligands are carboxylates, which show high stability to common impurities such as water/alcohols, as would be expected on the basis of pKₐ values.

In order to fully investigate the influence of water tolerance, a series of experiments were conducted using a mechanically stirred stainless-steel autoclave (CO₂ pressures 10−40 bar, Table 5). Once again, it is important to note that these conditions are not optimized for catalyst performance but rather were conducted under typical and highly consistent laboratory conditions. These experiments revealed that, with efficient mechanical stirring but without any further process optimization, 3 can already exhibit outstanding performance that far exceeds the best results reported to date using these catalysts. In addition to high productivities and activities, catalyst 3 retains excellent selectivity at loadings considerably lower than those that had previously proved effective (vs experiments in standard laboratory glassware) (vide supra). Increasing the pressure from 10 to 40 bar (compare entries B and C) results in only a marginal reduction in rate, consistent with previous rate studies and presumably due to a relative dilution of monomer. Additionally, it is clear that 3 can also show much higher tolerance to water than is found for reactions in glassware; indeed, up to 400 equiv of water can be added in these reactor runs, at very low catalyst loadings, while maintaining excellent activity and selectivity. Furthermore, the molecular weights of the PCHC can be increased under these conditions, even in the presence of 48 equiv of water (entries B and C).

**CONCLUSIONS**

This work clearly demonstrates the utility of the previously reported 2Zn₂ complexes (1 and 2) and, in particular, Mg₂ complex 3, as viable catalysts for the production of poly-(cyclohexene carbonate) polyols using CO₂ obtained from post-combustion CCS. Furthermore, these studies also highlight the tolerance of 3 to various impurities commonly found in captured carbon dioxide. It is notable that the catalyst continues to perform well even under high loads of model contaminants, including compounds bearing S=H (H₂S, octadecanethiol), N=H (diethyamine, MEA), and O=H (H₂O, MEA, SO₂) functional groups. Under the best conditions tested, catalyst activity exceeds 5000 h⁻¹ in the presence of excess added water (∼192 molar equiv vs catalyst). It is worth noting that the best conditions tested (mechanically stirred batch reactor, 10 bar, and 100 °C) are closely related to those used in the current industrial production of polyols. As expected, the molecular weights decrease with increasing water, or protic impurity, content, due to the chain transfer effect. However, this facilitates the selective production of low-molecular-weight polyols which could be suitable for further application in polyurethane manufacture. These findings demonstrate the potential for this polymerization catalysis to integrate with carbon capture and to apply contaminated carbon dioxide as a raw material for polymer synthesis.

** EXPERIMENTAL SECTION**

All reactions were conducted in a nitrogen-filled glovebox or using standard Schlenk techniques. All glassware was dried at 160 °C for 20 h and cooled under vacuum prior to use. Catalysts 1, 2, and 3 were prepared by previously reported procedures and stored under nitrogen. Cyclohexene oxide was purchased from Alfa Aesar (98%) and fractionally distilled from CaH₂. Diethylamine (anhydrous) and octadecanethiol were purchased form Sigma-Aldrich and used as received. High-purity CO₂ (5.0 grade) was obtained by passing industrial grade CO₂ (BOC gases) through a high-performance purifier (Valco Instruments). Reclaimed CO₂ was received from Ferrybridge Power Station on August 20th, 2013. Ferrybridge operates a CCS demonstration plan using amine-based post-combustion capture technologies. The CCS plant extracts up to 100 tons of CO₂/day from a coal-fired power station flue gas stream. More details regarding the typical operating parameters of amine-based carbon capture and separation technologies, including process schemes, can be found in ref 1. These processes typically comprise absorption of the gases by the liquid amine based solvent system, followed by desorption of the gases and solvent regeneration. The desorption processes typically involves a thermal treatment to accelerate the desorption of the carbon dioxide. The gas used from Ferrybridge was taken directly after desorption, and its pressure was approximately 1 bar. Data concerning typical carbon dioxide purity for post-combustion CCS can be found in Table 1 and in refs 1b, 17a, and 19a.

The samples were stored in Tedlar bags (with a volume of 10 L) each and at Econic Technologies were connected to the reaction apparatus via tubing, the entire system then being purged thoroughly with the sample gas. As a compression system was not available, a weight (~2 kg) was applied to compress the bag and ensure a positive pressure of gas at all times in the apparatus. Food grade CO₂ was obtained from ISG and dispensed into a balloon reservoir. CO₂ containing 500 ppm of SO₂ was prepared by BOC using high-purity CO₂ and was used as received. A CO₂ feed containing 0.63% water was prepared by heating 0.32 mL of water and 50 bar of high-purity CO₂ in a 2 L reactor held at 150 °C.

1H and 13C{1H} NMR spectra were measured on a Bruker AV-400 instrument, unless otherwise stated. All mass spectrometry measurements were performed using a Fisons Analytical (VG) Autospec spectrometer. MALDI-TOF MS experiments were carried out using a dithranol matrix in THF at a loading of 1:5 with KOAc as the cationizing agent. SEC data were collected using an Agilent 1260 infinity instrument, with THF as the eluent, at a flow rate of 1 mL min⁻¹. Two Agilent Mixed E columns were used in series. Narrow M₅₅ polystyrene standards were used to calibrate the instrument.

Polymerizations Conducted at Low Pressures. The appropriate quantity of catalyst (0.049 mmol) was weighed into a Schlenk tube, fitted with a magnetic stirrer, inside the glovebox. The tube was connected to a Schlenk line. Cyclohexene oxide (49 mmol, 5 mL) was added, via syringe, under a positive pressure of nitrogen. The tube was briefly degassed and then immediately refilled with CO₂ from the appropriate source, immersed in a pre-heated, stirred oil bath (defined as f₀), and maintained at the required temperature, with magnetic stirring at 750 rpm, for the duration of the reaction. At the end of the polymerization the reaction mixture was sampled via syringe while still hot and vigorously stirred (defined as fₛₕₜₐ) and an aliquot was analyzed by SEC and ¹H NMR spectroscopy. Any additives used in these experiments that were not present in the gas feed were weighed and added directly to the Schlenk tube inside the glovebox.

High Pressure Polymerizations. These reactions were conducted in a 1.8 dm³ stainless steel reactor equipped with a mechanical anchor impeller with Teflon blades. Gaseous (CO₂) and liquid (CHO, water) reactants were fed via valve ports in the reactor lid. Defined amounts of the catalyst and CHO were loaded into a pressure-tight steel cylinder in the glovebox, and the cylinder was then attached to...
the sealed, purged (CO2) reactor (at room temperature), heated to the required temperature, and pressurized to the required pressure (defined as t_{exit}). The pressure drop was monitored throughout, and CO2 was repeatedly added to the reactor during polymerization to maintain a constant pressure. The polymerization was stopped by releasing the CO2 pressure (over ca. 5 min, defined as t_{final}). CHO was removed in vacuo (pulsed vacuum), and the crude product was dried with N2 flushing. The crude product was weighed and analyzed by SEC and 1H NMR spectroscopy. Calculation of the total polymer yield for the reaction at the sampling time was based on the overall isolated yield and 1H NMR composition analysis of the withdrawn sample. Calculation of the final yield did not take into account the NMR sample, as this was deemed to be of negligible quantity and was constant across the series of experiments.

**ASSOCIATED CONTENT**

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501798s.

MALDI spectra of the polycarbonates (PDF)

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Notes

The authors declare the following competing financial interest(s): C.K.W. is a director and founder of Econic Technologies. Econic Technologies seeks to commercialize polymers from carbon dioxide.

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(20) The composition of this CO₂ was not analyzed but is specified at >99.5% by the manufacturers. The principal contaminants are expected to be water and oxygen.

(21) Such low molecular weights are at the lower limit of the calibration of our SEC instrument, and thus only estimates are given on the basis of chromatograms within the calibrated region.

(22) Although the specific SO₃ tolerance could not be tested in isolation, the post-combustion reclaimed gas (vide supra) was not found to contain SO₃. Despite the precedent for using SO₃ as a contaminant in related studies (see ref 15), we found that addition of even milligram quantities of either SO₃ or H₂SO₄ to mixtures of 3 and CHO resulted in a vigorous exotherm, a blackening of the solution, and the formation of black smoke that presumably results from the rapid acid-catalyzed polymerization/decomposition of CHO and/or 3. We do not recommend ever mixing these components.

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