Polyketones from Carbon Dioxide and Ethylene by Integrating Electrochemical and Organometallic Catalysis

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ABSTRACT: The utilization of carbon dioxide in polymer synthesis is an attractive strategy for sustainable materials. Electrochemical CO_2 reduction would offer a natural starting point for producing monomers, but the conditions of electrocatalysis are often drastically different from the conditions of organometallic coordination-insertion polymerization. Reported here is a strategy for integrating electrochemical and organometallic catalysts that enables polyketone synthesis from CO_2 and ethylene in a single multicompartment reactor. Polyketone materials that are up to 50% derived from CO_2 can be prepared in this way. Potentiostatic control over the CO-producing catalyst enables the controlled generation of low-pressure CO, which in conjunction with a palladium phosphine sulfonate organometallic catalyst enables copolymerization to nonalternating polyketones with the CO content tuned based on the applied current density.
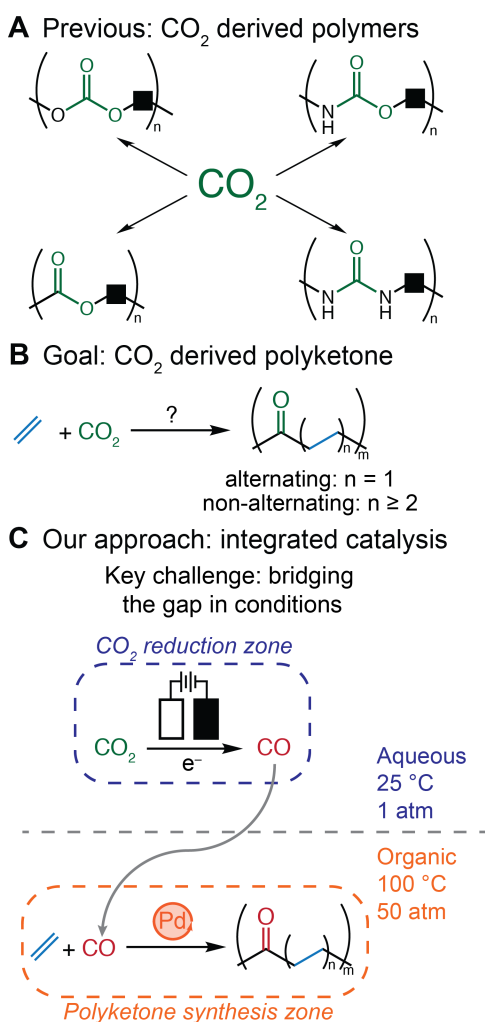
The majority of synthetic plastics, adhesives, and other polymer materials are derived from fossil fuels. The environmental consequences are significant, as preparation of monomers releases large amounts of CO_2 to the atmosphere.[1, 2] To address this challenge, scientists have long sought to utilize carbon dioxide as the source of carbon (and possibly oxygen) in polymer synthesis.[3] Polycarbonates prepared via copolymerization of CO_2 and epoxides represent a major success story in this area.[4-8] As shown in **Figure 1A**, routes from CO_2 to polyurethanes and polyureas have also been developed. Related chemistry incorporating CO_2 into polyolefins is at a nascent stage, with CO_2/butadiene copolymers comprised of 29 wt% CO_2 representing a recent breakthrough.[9-15] However, general strategies for accessing high-performance olefin-based polymeric materials from CO_2 are lacking.

Polyketone materials[16-18] attracted our attention as a possible target for improving sustainability in polymer synthesis. The copolymer of carbon monoxide and ethylene with a perfectly alternating microstructure (referring to the orientation and ordering of the monomer subunits), 1-oxo-trimethylene, is a prototypical polyketone. Prepared most commonly using molecular palladium catalysts, 1-oxo-trimethylene materials have many properties associated with attractive engineering thermoplastics, such as high melting points, excellent impact performance, and sturdy chemical resistance.[19] A few catalysts also produce "nonalternating" polyketones under specific conditions (elevated temperature, low CO pressure relative to ethylene pressure) that feature several ethylene units between each carbonyl group.[20-22] These materials have lower melting temperatures and improved solubility, which can enhance processability.[7] At extremely low CO incorporation, nonalternating polyketone behaves more like polyethylene, a material for which mass production infrastructure is already in place.[7, 8] A recent study demonstrated nickel-catalyzed CO/C_2H_4 copolymerization with as little as 0.3 mol% CO content, accessing materials that could be processed like polyethylene while also featuring facile

degradation pathways due to the isolated ketone functional groups.[8]

To date, polyketones have been prepared from CO and C_2H_4, which are industrially sourced from fossil fuel feedstocks. This process is typically run under high pressures of CO, which can pose safety concerns due to its high toxicity. Methods for the sustainable production of CO have been developed,[23-25] but there is an opportunity to develop the fundamental catalysis tools needed to integrate electrochemical CO_2 reduction with organometallic polymerization catalysis (**Figure 1B**). Initial progress has been made in this area, albeit in low pressure applications.[26-28] Often times, however, electrochemical and organometallic catalysts require starkly different reaction conditions for optimal performance. The electroreduction of CO_2 typically employs an aqueous electrolyte at room temperature and 1 bar CO_2,[29-31] while palladium-catalyzed polyketone synthesis typically utilizes organic solvents at elevated temperatures (>80 °C) and high pressures (>20 bar).[19, 32, 33]

A Previous: CO_2 derived polymers

B Goal: CO_2 derived polyketone

alternating: n = 1
non-alternating: n ≥ 2

C Our approach: integrated catalysis

Key challenge: bridging the gap in conditions

CO_2 reduction zone

Aqueous
25 °C
1 atm

Organic
100 °C
50 atm

Polyketone synthesis zone

Figure 1. Previous non-integrated polyketone synthesis reactions and our proposed electrochemical/organometallic integrated method.

Polyketone materials in which each carbonyl unit is derived from carbon dioxide are reported here, accessed through the integration of heterogeneous electrocatalytic

CO_2 reduction to CO and homogeneous organometallic CO/C_2H_4 copolymerization catalysis in a multicompartment reactor (**Figure 1C**). Overcoming incompatibility challenges through reactor design and development of suitable reaction conditions enables the synthesis of perfectly alternating polyketone (1-oxo-trimethylene) that is *50 wt% CO_2-derived by mass*. With a different organometallic palladium complex in the same integrated catalysis reactor, nonalternating polyketones were prepared *with the extent of CO_2-derived carbonyl linkages controlled electrochemically*.

We began by considering how to achieve the challenging task of identifying conditions where electrochemical and organometallic catalysts could be coupled. The solvent, temperature, and pressure conditions were considered key factors.

Initial studies sought nonaqueous CO_2 electroreduction using heterogeneous metal electrodes. High activity and fewer chain transfer events were observed in organic solvents during polyketone synthesis catalyzed by organometallic Pd complexes, relative to aqueous conditions.[19, 32, 33] However, data on electrochemical CO generation from CO_2 in nonaqueous solvents is limited.[34-36] Three polar aprotic solvents were tested: 1,2-dichloroethane (1,2-DCE), 1,2-difluorobenzene (1,2-DFB), and *N,N*-dimethylformamide (DMF), all with the addition of 5% v/v methanol (MeOH) as a proton donor and 0.25 M tetrabutylammonium hexafluorophosphate (TBAPF6) as an electrolyte (**Table 1**). Gold is amongst the most CO selective catalysts in aqueous electrolytes,[37, 38] so we were surprised to find that gold sputtered on carbon paper or supported on titanium did not produce detectable amounts of CO in 1,2-DCE, 1,2-DFB, or DMF (**Table S1**). Thus, the need for a nonaqueous solvent for the organometallic reaction motivated us to develop an alternative to the standard CO_2 reduction electrocatalyst materials that would work well in organic solvents.
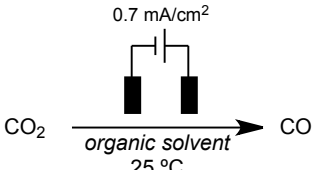
Palladium foil showed promising results for CO_2 electroreduction in nonaqueous media (**Table 1A** and **Table S1** in the SI). Room temperature constant current electrolysis in each of the three aforementioned co-solvent systems was performed with a Pd foil working electrode. The Faradaic efficiency for CO_2 reduction to CO (FE_{CO}) after 24 h was only ca. 1% in 1,2-DFB, as quantified by online gas chromatography (GC). Although the FE_{CO} increased to 2.5% in 1,2-DCE, this solvent was problematic because of a competing hydrodechlorination reaction that produced C_2H_4 and C_2H_6 (observed via GC analysis).[39, 40] DMF with 5% v/v MeOH was more promising, with CO formed in the 8-19% FE_{CO} range. Using DMF without added MeOH led to even higher selectivity, 35-44% FE_{CO}, and thus, these conditions were chosen for further studies. The FE_{CO} in DMF was higher than reports of Pd foil in water (FE_{CO} = 13%)[41-43] and similar to Pd foil in methanol (FE_{CO} ~ 40%).[41-44]

Having identified promising conditions for nonaqueous CO generation, we turned to two classic organometallic CO/C_2H_4 copolymerization catalysts. Some of the first reports of organometallic polyketone synthesis utilized 1,2-bis(diphenylphosphino)propane (dppp),[32, 45] so we prepared the cationic palladium methyl complex [(dppp)Pd(Me)(MeCN)][BAr$^F_4$] (**Pd-PP**, Ar^F is 3,5-bis(trifluoromethyl)phenyl).[46] This catalyst produces

perfectly alternating 1-oxo-trimethylene (ca. 1 "mistake" per 10^5 insertions).[47] The neutral catalyst $(PO)Pd(Me)(pyridine)$ (**Pd-PO**, PO is $o\text{-}Ar_2PC_6H_4SO_3$ with Ar being $o\text{-}MeO\text{-}C_6H_4$) was the first catalyst reported to furnish nonalternating polyketone.[16, 17] Alkyl complexes with weakly bound MeCN and pyridine ligands have been shown to initiate polymerization without requiring any chemical activator, and to carry out the individual polymerization steps at low temperatures.[16, 47]
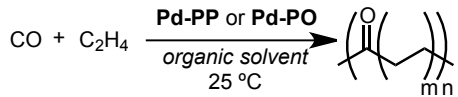
Table 1. Selected experiments independently optimizing reaction conditions for CO_2 reduction and copolymerization. (A) Electrochemical CO_2 reduction in nonaqueous solvent at low temperature. (B) CO/C_2H_4 copolymerization in nonaqueous solvent at low temperature.

A

$$CO_2 \xrightarrow[\substack{\text{organic solvent} \\ 25\ °C}]{0.7\ mA/cm^2} CO$$

Elect-rodes	Solvent	Time (h)	P_{CO_2} (bar) initial	P_{C2H4} (bar) initial	FE_{CO} (%)	P_{CO} (bar) final
Au-Ti	DMF (10% MeOH)	2	8	15	7	0.008
Pd	DMF (5% MeOH)	3	7	7	19	0.028
Pd	DMF (5% MeOH)	12	7	7	5	0.032
Pd	DMF	24	7	7	44	0.531
Pd	1,2-DCE (5% MeOH)	24	5	5	3	0.002

B

$$CO + C_2H_4 \xrightarrow[\substack{\text{organic solvent} \\ 25\ °C}]{\textbf{Pd-PP or Pd-PO}} \text{polymer}$$

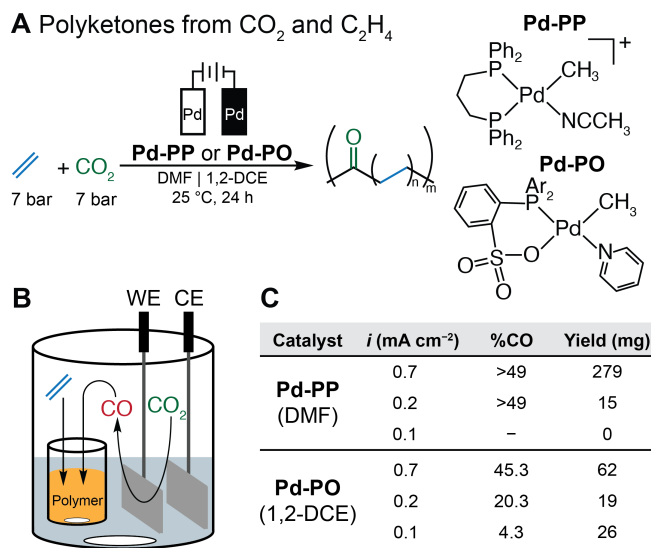| Catalyst	Solvent	P_{CO} (bar)	P_{C2H4} (bar)	Activity (g mmol^{-1} h^{-1})	M_n (Đ)
Pd-PO	1,2-DCE	0.5	0.5	0	-
Pd-PO	1,2-DCE	0.5	7	0.064	3581 (1.8)
Pd-PO	1,2-DCE	10	10	0.105	6381 (1.5)
Pd-PO	DMF (40 °C)	0.5	10.5	0.27	-
Pd-PP	1,2-DCE	0.5	0.5	0.197	-
Pd-PP	1,2-DCE	0.5	10	0.166	24160 (2.2) / 5068 (1.0) / 1931 (1.1)
Pd-PP	1,2-DCE	10	10	0.819	21370 (7.3)
Pd-PP	DMF	0.5	10	0.43	-

Focusing on room temperature copolymerization, we subjected **Pd-PP** and **Pd-PO** to a range of conditions, varying solvent, catalyst loading, and reactant pressures. The findings are summarized in **Table 1** and **Tables S2–S4**. Polymer is still formed at 0.5 bar each of CO and C_2H_4 at room temperature in reactions catalyzed by **Pd-PP**. In contrast, the neutral catalyst **Pd-PO**, which generally exhibits lower activity than **Pd-PP**, did not form any

polymer at 1 bar total pressure. At 0.5 bar CO and 7 bar C_2H_4, however, appreciable polymerization activity was apparent. Neither H_2 nor CO_2 gas interfered with the copolymerization, confirming that these byproduct or reactants from the electrocatalytic reaction do not inhibit the copolymerization.

Based on these studies, we targeted 7 bar C_2H_4 for integration with electrochemical CO generation. A bespoke high-pressure electrochemical reactor was capable of supplying varying pressures of CO_2 and C_2H_4 was designed (Figure S1). It was hypothesized that higher pressures of CO_2 would increase CO yield, as the mass transport of CO_2 to the Pd foil working electrode is assumed to be the limiting step for CO_2 reduction. Initial high-pressure electrolysis efforts in DMF (without added MeOH) at an applied current density of 0.7 mA/cm^2 for 3 h under a total pressure of 14 bar with a 1:1 CO_2 : C_2H_4 ratio produced CO (P_{CO} = 0.03 bar, FE_{CO} = 19%). Extending the electrolysis time to 24 h under otherwise identical conditions increased P_{CO} to 0.53 bar with a FE_{CO} = 44%. Based on the CO/C_2H_4 copolymerization studies described above, this pressure of CO was expected to be sufficient for integration with the organometallic catalysts.

Initial attempts to integrate the two reactions under mutually optimized conditions were thwarted by the electroreductive instability of the organometallic Pd complexes. Cyclic voltammograms collected in DMF with 0.25 M TBAPF$_6$ on a glassy carbon working electrode revealed irreversible reductions for **Pd-PP** ($E_{p,c} \sim -2.9$ V vs ferrocenium/ ferrocene, Fc$^+$/Fc) and **Pd-PO** ($E_{p,c} \sim -2.48$ V vs Fc$^+$/Fc) (Figure S2). These reduction potentials are unfortunately more positive than what is required to reach 0.7 mA/cm^2 electrolysis current density for CO production (-3.71 V vs. Fc$^+$/Fc). As such, experiments wherein the electrochemical reactor was charged with DMF/ TBAPF$_6$ electrolyte containing the 5 mM of either Pd complex resulted in extensive formation of Pd black with only traces of polymer.

To combat the degradation of the polymerization catalyst under CO_2 reduction potentials, a vial-in-a-vial approach was adopted as depicted in **Figure 2**. Taking advantage of the intermediate CO being a gas, the electrocatalytic material and molecular catalyst were physically separated in beakers under a shared headspace in the pressure reactor.

A Polyketones from CO_2 and C_2H_4

7 bar + CO_2 7 bar — **Pd-PP** or **Pd-PO** — DMF | 1,2-DCE, 25 °C, 24 h

B WE CE

C

Catalyst	i (mA cm^{-2})	%CO	Yield (mg)
Pd-PP (DMF)	0.7	>49	279
	0.2	>49	15
	0.1	–	0
Pd-PO (1,2-DCE)	0.7	45.3	62
	0.2	20.3	19
	0.1	4.3	26

Figure 2. Synthesis of polyketones from CO_2 and C_2H_4. (A) Reaction scheme and catalyst structures. (B) Reactor design showing outer compartment (DMF solution depicted in blue) with electrochemical components and inner compartment (DMF or 1,2-DCE solution containing organometallic Pd catalyst, depicted in yellow).

The high-pressure reactor containing DMF and 0.25 M TBAPF$_6$ as electrolyte and a vial of DMF containing **Pd-PP** was charged with 7 bar CO_2 and 7 bar C_2H_4, and a current density of 0.7 mA·cm^{-2} was applied for 24 h at room temperature while both chambers were stirred. CO was produced (FE$_{CO}$ = 37%) with a similar efficiency to electrolyses in the absence of the polymerization catalyst (**Table S5**). An off-white precipitate was observed in the vial containing **Pd-PP** at the end of the reaction. The solid was isolated, washed with acidified MeOH and characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, attenuated total reflectance infrared spectroscopy (ATR-IR) spectroscopy, and size exclusion chromatography (SEC). The NMR and IR spectra of the polyketone samples are consistent with a perfectly alternating microstructure (>49% CO content), as expected for the type of catalyst employed. ATR-IR spectra for each polymer sample featured a C=O stretch at 1692 cm^{-1}, consistent with alternating polyketone (>49% CO incorporation).[7] In these initial experiments, we chose DMF for the solvent in both compartments of the reactor. The polymer yield was comparable when DMF was used for the electrochemical compartment and 1,2-DCE was employed in the copolymerization compartment (**Table S5**). NMR analysis in a 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/C$_6$D$_6$ (4:1) mixture reveals the diagnostic signatures of perfect alternation of ethylene and carbonyl units.[16] The SEC traces (HFIP eluent) show that the polymers produced via integrated catalysis have similar molecular weight as those produced from CO (**Table S2**), with high-dispersity number average molecular weights (M_n) in the range of 4,000-18,000 g/mol and sometimes featuring multimodal distributions (**Table S5**). The high-pressure electrochemical reactor and reaction conditions overcome apparent incompatibility to enable the dual

electrochemical/organometallic catalytic synthesis of polyketone that *is 50% CO_2-derived by weight*.

Next, we decided to explore the possibility of electrochemical control over co-monomer concentration by varying of the applied current density to the Pd foil cathode. Using **Pd-PP** as the organometallic catalyst, the applied current density was varied from 0.7 to 0.1 mA·cm^{-2}. The yield drops as the current density is lowered, correlating with a drop in P_{CO} at the end of electrolysis (from 0.45 to 0.01 bar, **Figure 2**). In cases where polymer formed, it was perfectly alternating polyketone (>49% CO incorporation). No polymer was observed at the lowest current density.

The same reactor was next employed for reactions using **Pd-PO**, a catalyst previously reported to produce nonalternating polyketones (typical conditions are 110 ºC, P_{C2H4} = 30 bar, P_{CO} = 5 bar).[17, 21, 48, 49] The high-pressure reactor was charged with DMF and 0.25 M TBAPF$_6$ in the main electrochemical compartment and 1,2-DCE containing **Pd-PO** in the polymerization compartment, and pressurized to 7 bar CO_2 and 7 bar C_2H_4. A current density ranging from 0.7 to 0.1 mA·cm^{-2} was applied for 24 h at room temperature. A precipitate formed in the inner vial holding the organometallic catalyst. The materials were isolated but exhibited poor solubility in HFIP, an initial indication the polymer was distinct from that produced by **Pd-PP**. As the degree of CO incorporation in the polyketone copolymer decreases, solubility in HFIP decreases, but solubility in 1,1,2,2-tetrachloroethane (TCE) increases. NMR spectra were thus collected in both TCE-d_2 at 100 °C and HFIP at 25 °C to allow for a comprehensive microstructure analysis. NMR spectral analysis was consistent with the formation of materials with a variable microstructure.

At 0.5 and 0.7 mA·cm^{-2} applied current density, where 0.25-0.5 bar partial pressures of CO were generated, polymers with predominantly alternating microstructure were produced in integrated catalysis featuring **Pd-PO**. But at 0.3 mA·cm^{-2} applied current density and below, where the CO partial pressure was as low as 0.002 bar after the reaction, the NMR spectra show signals for multiple repeating C_2H_4 units diagnostic of nonalternating polyketone. **Figure 3** reveals correlated trends in the %CO incorporation determined by NMR spectroscopy and the C=O stretches observed by ATR-IR spectroscopy as a function of applied current density (and CO generated during electrolysis). The polymers ranged from almost perfectly alternating (>45% CO) when the CO pressure approached 0.5 bar, to very low CO content of 3-6% when less than 0.01 bar CO was present. The potentiostat therefore provides a means of fine-tuning the degree of CO incorporation in the polymer.

The NMR and IR spectroscopic data, along with SEC data showing a monomodal distribution of polymer molecular weights, point to nonalternating polyketone materials, rather than mixtures of polyethylene and alternating polyketone. Further support comes from DOSY NMR spectra, which show that the resonance for CH$_2$ repeat units far from ketone groups have the same diffusion coefficient as the CH$_2$ units adjacent to ketone units, confirming they are part of the same nonalternating polyketone polymer. We prepared authentic samples of both a alternating polyketone / polyethylene block copolymer and a physical

blend of alternating polyketone and polyethylene produced by these catalysts, and the NMR and IR signatures are distinct (SI Figure X). Although **Pd-PO** does catalyze slow ethylene homopolymerization at room temperature under 7 bar C_2H_4 (**Table S6**) we hypothesize that even the small amounts of CO formed at early times effectively inhibit any of this potential side reaction.
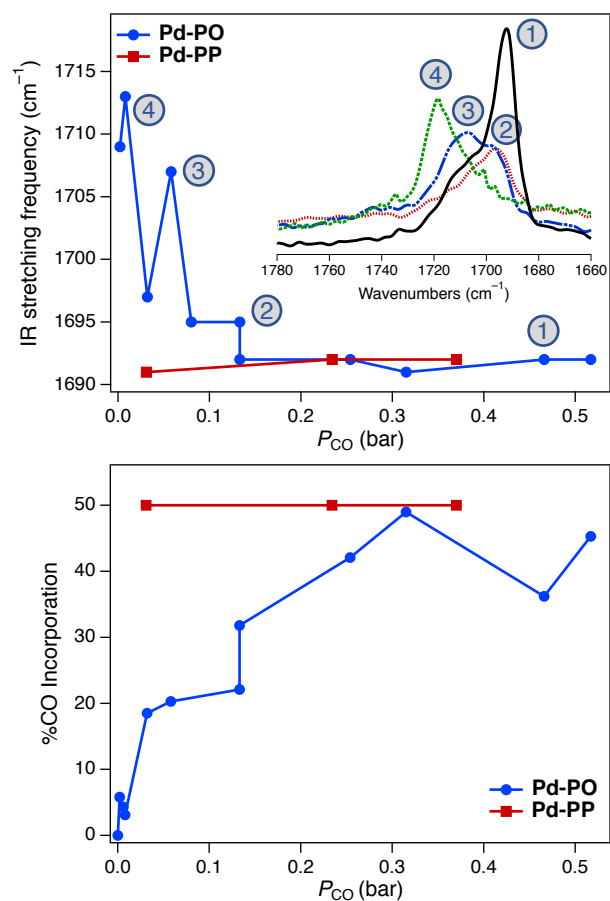
Figure 3. CO incorporation (%) and C-O stretching frequency (top) plotted as a function of the CO partial pressure for each catalyst used (bottom). The partial pressure of CO is modulated by the applied current density.

The generation of nonalternating polyketone at room temperature by **Pd-PO** in the integrated system was rather surprising. When 0.5 bar CO was used directly in copolymerizations under otherwise similar conditions, the %CO incorporation was 47.3% at 25 °C; even at just 0.1 bar (produced by charging with 1 bar CO, then pressurization to 9 bar N_2 and venting), the material was predominantly *alternating* polyketone (43.6% CO, $\nu_{CO} = 1692$ cm^{-1}). Only at elevated temperatures (40-100 °C), with a 20:1 C_2H_4:CO ratio in the gas feed, was a reduction to below 20% CO incorporation observed (**Table S4**). We attribute the ability to generate nonalternating polymer to the controlled production of small amounts of CO using electrochemistry. Although it can be difficult to add small amounts of CO accurately using traditional batch reactor methods, an electrochemical integrated system shows that low CO levels are easily achieved and nonalternating materials can be prepared in one pot from CO_2. The nonalternating polyketone materials with varying degrees of CO_2-derived

linkages have been recognized as promising materials for polyolefin applications because they are more readily degraded than polyethylene itself.[8, 22, 50-52]

The physically separated beakers, applied current to the Pd foil working electrode, and CO_2 and C_2H_4 gasses are all necessary for polymer formation. When the organometallic Pd catalysts were dissolved directly in the electrolyte solution, the organometallic catalysts decomposed and the Pd foil was deactivated, preventing polymerization (vide supra, **Table S5**). Either in the absence of an external applied current or when N_2 is substituted for CO_2, integrated catalysis with **Pd-PP** yielded no precipitate while **Pd-PO** catalyzed the homopolymerization of C_2H_4 (**Table S6**). Integrated trials using $^{13}CO_2$ as a pre-monomer yielded a dramatically intensified ^{13}C NMR peak at ~212 ppm for the carbonyl carbon of the polyketone product (Figure SX).

Integrating electrochemical and organometallic catalysis enables the synthesis of CO_2-derived polyketones. This report provides a blueprint for approaching the challenge of catalyst integration for seemingly incompatible reaction conditions, using a unique reactor design and systematic variation of reaction parameters to achieve suitable conditions for co-catalysis. Furthermore, integrated catalysis produces polyketone materials of variable composition, with the molecular weight and degree of CO incorporation controlled by the choice of organometallic catalyst and applied current density, offering new opportunities in sustainable polymer synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

> Electrochemistry details, polymerization and characterization data, NMR and IR spectra, SEC traces (PDF)

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ACKNOWLEDGMENT

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