

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 CO₂ reduction would offer a natural starting point for producing monomers, but the conditions of electrocatalysis are often drastically different from the conditions of coordination-insertion polymerization. Reported here is a strategy for coupling electrochemical and organometallic catalysts that enables polyketone synthesis from CO₂ and ethylene in a single multicompartiment reactor. Polyketone materials that are up to 50% derived from CO₂ 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 CO₂ 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 (**Figure 1A**).³ Polycarbonates prepared via copolymerization of CO₂ and epoxides represent a major success story in this area.⁴⁻⁸ Routes from CO₂ to polyurethanes and polyureas have also been developed.³ Chemistry combining CO₂ and olefins is nascent, with CO₂/butadiene copolymers (29 wt% CO₂) representing a recent breakthrough.⁹⁻¹⁵ However, general strategies for accessing high-performance olefin-based polymeric materials from CO₂ are lacking.

Polyketone materials¹⁶⁻¹⁸ 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), poly(1-oxo-trimethylene), is a prototypical polyketone. Prepared most commonly using molecular palladium catalysts, poly(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}

To date, polyketones have been prepared from CO and C₂H₄, which are industrially sourced from fossil fuels. This process is typically run under high pressures of CO, which

can pose safety concerns due to its high toxicity. Methods for sustainable CO production have been developed,²³⁻²⁵ but there is an opportunity to improve efficiency by developing the fundamental catalysis tools needed to integrate electrochemical CO₂ reduction with organometallic polymerization catalysis (**Figure 1B**). Initial progress has been made in this area, albeit in low pressure applications,²⁶⁻²⁸ or generating CO from CO₂ using thermal reactions.²⁹ Often times, however, electrochemical and organometallic catalysts require starkly different reaction conditions for optimal performance. The electroreduction of CO₂ typically employs aqueous solutions at room temperature and 1 bar CO₂,³⁰⁻³² while palladium-catalyzed polyketone synthesis typically utilizes organic solvents at elevated temperatures (>80 °C) and high pressures (>20 bar).^{19, 33, 34}

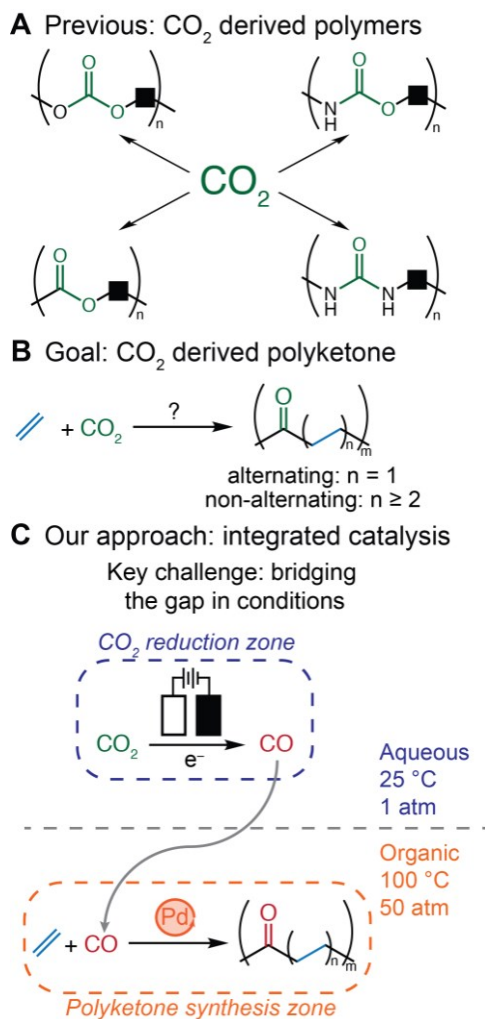


Figure 1. Previous non-integrated polyketone synthesis reactions and our proposed electrochemical/organometallic integrated method.

Polyketone materials in which each carbonyl unit is derived from carbon dioxide are reported here, accessed through the integration of heterogeneous electrocatalytic CO₂ reduction to CO and homogeneous organometallic CO/C₂H₄ copolymerization catalysis in a multicompartiment reactor (**Figure 1C**). Overcoming incompatibility challenges through reactor design and development of suitable reaction conditions enables the synthesis of

perfectly alternating polyketone that is 50 wt% CO₂-derived by mass. With a different organometallic palladium complex in the same integrated catalysis reactor, nonalternating polyketones were prepared with the extent of CO₂-derived carbonyl linkages controlled electrochemically.

We began by identifying reaction conditions where electrochemical and organometallic catalysts could be coupled. The solvent, temperature, and pressure conditions were considered key factors. Initial studies focused on nonaqueous CO₂ 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, 33, 34} However, data on electrochemical CO generation from CO₂ in nonaqueous solvents is limited.³⁵⁻³⁷ 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 1A**). A bespoke high-pressure electrochemical reactor capable of supplying varying pressures of CO₂ and C₂H₄ was designed in order to enhance CO yield and limit mass transport limitations (Figure S5).

Gold is amongst the most CO selective electrocatalysts in aqueous electrolytes,^{38, 39} so we were surprised to find that gold sputtered on carbon paper or supported on titanium produced almost no CO in 1,2-DCE, 1,2-DFB, or DMF as quantified by online gas chromatography (GC) (**Table S1**). Palladium foil showed more promising results for CO₂ electroreduction in nonaqueous media (**Table 1A and S1**). The Faradaic efficiency for CO₂ reduction to CO (FE_{CO}) after 24 h was only ca. 1% in 1,2-DFB. Although the FE_{CO} increased to 2.5% in 1,2-DCE, this solvent was problematic because of a competing hydrodechlorination reaction that produced C₂H₄ and C₂H₆ (observed via GC analysis).^{40, 41} DMF with 5% v/v MeOH was more promising, with CO formed in the 5-19% FE_{CO} range. Using DMF containing trace H₂O but no added MeOH led to even higher selectivity, 35-44% FE_{CO}, and extending the reaction time results in ca. 0.5 bar CO produced. These conditions were chosen for further studies. The FE_{CO} in DMF was higher than reports of Pd foil in water (FE_{CO} = 13%)⁴²⁻⁴⁴ and similar to Pd foil in methanol (FE_{CO} ~ 40%).⁴²⁻⁴⁵ Concomitant hydrogen evolution due to trace H₂O was also observed in these CO₂ electrolyses experiments, with faradaic efficiencies (FE_{H₂}) ranging from 1 – 67% depending on the conditions (see Supporting Information Section S2.2 and Table S1 for more details). Despite the presence of H₂, no Pd-catalyzed hydrogenation of ethylene to ethane was apparent in GC traces of the headspace gas.

Having identified promising conditions for nonaqueous CO generation, we turned to two classic organometallic CO/C₂H₄ copolymerization catalysts (**Figure 2**). Some of the first reports of organometallic polyketone synthesis utilized 1,3-bis(diphenylphosphino)propane (dppp),^{34, 46} so the cationic palladium methyl complex $[(dppp)Pd(Me)(MeCN)][BAr^F_4]$ (**Pd-PP**, Ar^F is 3,5-bis(trifluoromethyl)phenyl) was prepared.⁴⁷ This catalyst produces perfectly alternating polyketone (ca. 1 “mistake” per 10⁵ insertions).⁴⁸ The neutral catalyst

(PO)Pd(Me)(pyridine) (**Pd-PO**, PO is *o*-Ar₂PC₆H₄SO₃ with Ar being *o*-MeO-C₆H₄) was the first catalyst reported to furnish nonalternating polyketone.^{17, 18} Alkyl complexes with weakly bound MeCN and pyridine ligands have been shown to initiate polymerization without requiring any chemical activator at low temperatures.^{18, 48}

Table 1. Selected experiments independently optimizing reaction conditions for CO₂ reduction and copolymerization. (A) Electrochemical CO₂ reduction in nonaqueous solvent at low temperature. (B) CO/C₂H₄ copolymerization in nonaqueous solvent at low temperature.

A

Electrodes	Solvent	Time (h)	<i>P</i> _{CO₂} (bar) initial	<i>P</i> _{C₂H₄} (bar) initial	FE _{CO} (%)	<i>P</i> _{CO} (bar) final
Au-Ti	DMF (10% MeOH)	2	8	15	7	0.008
Pd	DMF	3	7	7	19	0.028
Pd	(5% MeOH)	12	7	7	5	0.032
Pd	(5% MeOH)	24	7	7	44	0.531
Pd	1,2-DCE (5% MeOH)	24	5	5	3	0.002

B

Catalyst	Solvent	<i>P</i> _{CO} (bar)	<i>P</i> _{C₂H₄} (bar)	Activity (g mmol ⁻¹ h ⁻¹)	<i>M</i> _n (Đ)
Pd-PO	1,2-DCE	0.5	0.5	0	-
Pd-PO	1,2-DCE	0.5	7	0.064	3580 (1.8)
Pd-PO	1,2-DCE	10	10	0.105	6380 (1.5)
Pd-PO	DMF (40 °C)	0.5	10.5	0.27	-
Pd-PP	1,2-DCE	0.5	0.5	0.197	-
					24160 (2.2)
Pd-PP	1,2-DCE	0.5	10	0.166	5070 (1.0)
					1930 (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 gas pressures. The findings are summarized in **Table 1B** and **S2-S4**. Although the activity is low, polymer is still formed at 0.5 bar each of CO and C₂H₄ 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 C₂H₄, however, appreciable polymerization activity was apparent. We tested whether H₂ and CO₂ gases present during electrolysis might interfere with the copolymerization; the activity was reduced by ca. 50% under 0.5 bar H₂, while the average polymer chain length was shortened by ca. 50% under 10 bar CO₂. The amount and molecular weight of polyketone, however, was still sufficient to proceed with integration of copolymerization with electrochemical CO generation.

The electrochemical reactor was charged with DMF/TBAPF₆ electrolyte containing 5 mM of **Pd-PP** or **Pd-PO** and held at constant current, but formation of Pd black was observed along with traces of polymer. Cyclic voltammograms collected in DMF with 0.25 M TBAPF₆ revealed irreversible reductions for **Pd-PP** (*E*_{p,c} ~ -2.9 V vs ferrocenium/ferrocene, Fc⁺/Fc) and **Pd-PO** (*E*_{p,c} ~ -2.48 V vs Fc⁺/Fc) (Figure S6). These reduction potentials are unfortunately more positive than what is required to reach the 0.7 mA/cm² electrolysis current density needed to generate sufficient amounts of CO for copolymerization (-3.71 V vs. Fc⁺/Fc).

To combat the degradation of the polymerization catalyst under CO₂ 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 under a shared headspace in the pressure reactor.

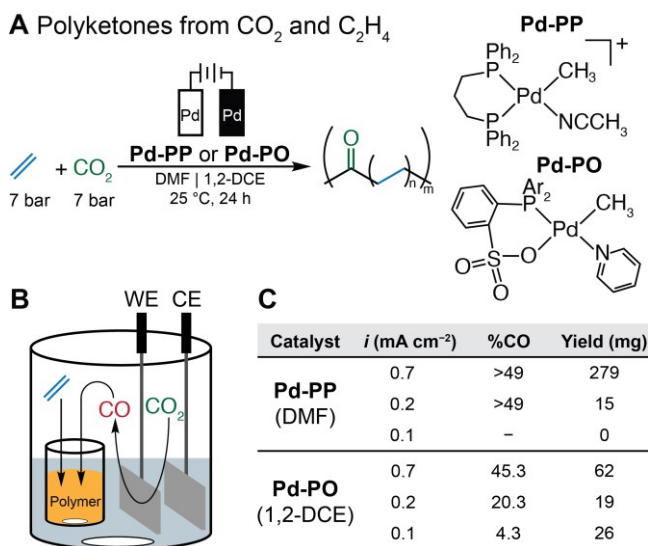


Figure 2. Synthesis of polyketones from CO₂ and C₂H₄. (A) Reaction scheme and catalyst structures (Ar = *o*-MeO-C₆H₄). (B) Reactor design showing outer compartment (DMF solution depicted in blue) with electrochemical components and inner compartment (DMF or 1,2-DCE solution containing organometallic Pd catalyst, depicted in orange).

The high-pressure reactor containing DMF and 0.25 M TBAPF₆ as electrolyte and a vial of DMF containing **Pd-PP** was charged with 7 bar CO₂ and 7 bar C₂H₄, 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 with a similar efficiency to electrolyses in the absence of the polymerization catalyst (37% FE_{CO} , **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 ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, attenuated total reflectance infrared (ATR-IR) spectroscopy, and size exclusion chromatography (SEC). NMR analysis in a 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/ C_6D_6 (4:1) mixture revealed the signatures of a perfectly alternating microstructure (>49% CO content), as expected for the type of catalyst employed.¹⁸ ATR-IR spectra for each polymer sample featured a $\text{C}=\text{O}$ 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**). The SEC traces (HFIP eluent) and NMR analysis of the degree of polymerization (DP) show that the polymers produced via integrated catalysis have similar molecular weight as those produced from CO, 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 mass.

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 $\text{mA}\cdot\text{cm}^{-2}$. The yield dropped as the current density was lowered and P_{CO} decreased (from 0.45 to 0.01 bar, **Figure 2**). In cases where polymer formed, it was perfectly alternating polyketone (>49% CO incorporation). Either in the absence of an external applied current or under N_2 instead of CO_2 , integrated catalysis with **Pd-PP** yielded no precipitate. Integrated trials using $^{13}\text{CO}_2$ as a monomer precursor yielded a dramatically intensified ^{13}C NMR peak at ~ 212 ppm for the carbonyl carbon of the polyketone (Figure S50).

The same reactor was next employed for reactions using **Pd-PO**, a catalyst previously reported to produce nonalternating polyketones (typical conditions are $110\text{ }^\circ\text{C}$, $P_{\text{C}_2\text{H}_4} = 30\text{ bar}$, $P_{\text{CO}} = 5\text{ bar}$).^{16, 17, 20, 21} The high-pressure reactor was charged with DMF and 0.25 M TBAPF₆ 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 $\text{mA}\cdot\text{cm}^{-2}$ was applied for 24 h at room temperature. At 0.5 and 0.7 $\text{mA}\cdot\text{cm}^{-2}$ 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 $\text{mA}\cdot\text{cm}^{-2}$ 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. 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 HFIP at $25\text{ }^\circ\text{C}$ and TCE- d_2 at $100\text{ }^\circ\text{C}$ for microstructure analysis.

Figure 3 reveals correlated trends in the %CO incorporation determined by NMR spectroscopy and the $\text{C}=\text{O}$ stretches observed by ATR-IR spectroscopy as a function of applied current density (and CO generated during electrolysis). The intensity and energy of the CO stretches in the IR spectra reflect the change in CO content in the polymers, with weaker, higher-energy stretches indicating the presence of nonalternating polymers, while lower energy bands are indicative of alternating polyketone.⁷ 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% at less than 0.01 bar CO. The potentiostat therefore provides a means of fine-tuning the degree of CO incorporation in the polymer.

It is important to distinguish between nonalternating polyketone and mixtures of polyethylene and alternating polyketone. 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 an 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 (Figure S27-S28). 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. Furthermore, chain end analysis is consistent with minimal chain transfer, preventing release of polyethylene before CO incorporation.

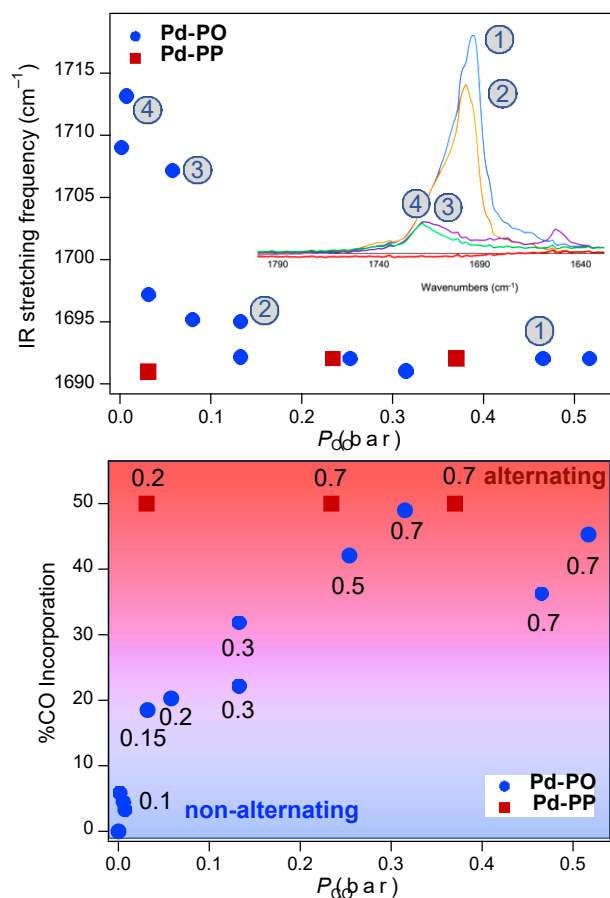


Figure 3. CO incorporation (%) and C-O stretching frequency (top) plotted as a function of the CO partial pressure for each catalyst used (bottom). The partial pressure of CO is modulated by the applied current density.

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 conditions similar to integrated catalysis, the %CO incorporation was 47%; even at just 0.1 bar (charging 1 bar CO, then 9 bar N₂ and venting), the material was predominantly *alternating* polyketone (44% CO, $\nu_{CO} = 1692\text{ cm}^{-1}$). Only at elevated temperatures (80–100 °C), with a 20:1 C₂H₄:CO ratio, did the CO content drop below 20% (**Table S4**). We attribute the ability to generate nonalternating polymer to the controlled production of small amounts of CO using electrochemistry. The integrated system readily produces the very low CO levels needed to access nonalternating materials in one pot from CO₂. Such materials are promising because they are more readily degraded than polyethylene itself.^{8, 22, 49–51}

Integrating electrochemical and organometallic catalysis enables the synthesis of CO₂-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. Although challenges remain, such as the low activity of the polymerization catalysts at room temperature and the low conversion of ethylene, these studies hint at 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

This material is based on work supported by National Science Foundation as part of the Center for Integrated Catalysis (CHE-2023955). The authors gratefully acknowledge Yohei Yoshinaka and Stephen A. Miller for assistance with size exclusion chromatography. BSN is grateful for an INFEWS fellowship (NSF Grant DGE-1735325).

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