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New Class of Catalysts for Alternating Copolymerization of Alkylene Oxide and Carbon Dioxide

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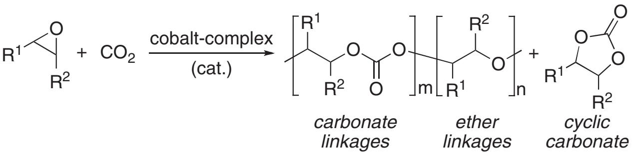
Di(ketoiminato)cobalt complexes have been employed for the alternating copolymerization of alkylene oxide and carbon dioxide. These complexes exhibited not only good catalytic activity for polycarbonate synthesis, but also an excellent selectivity for the formation of carbonate linkages without any ether linkage in the reaction of several alkylene oxides, especially for ethylene oxide.

Carbon dioxide has recently attracted considerable attention as one of the most reasonable C_1 feedstocks[1] because of its abundant and inexpensive availability as well as low toxicity. A promising source of carbon dioxide is ironworks and petroleum plants that exhaust large amounts of CO_2 gas. On the other hand, CO_2 has been suspected as a global warming factor due to its greenhouse effect. Based on these interests, much effort has been made on carbon dioxide fixation and transformation for sustainable development. Although several chemical processes have already been commercialized, such as the Kolbe–Schmitt reaction for Aspirin synthesis, various chemical fixations or transformations have recently been proposed to efficiently convert CO_2 into useful fine chemicals or commodity materials.[2]

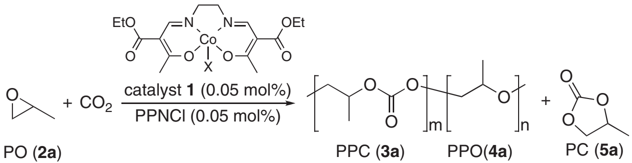
We have reported that in the presence of an optically active di(ketoiminato)cobalt(II) complex[3] as a catalyst, CO_2 was employed as a reactant for *racemic* epoxides to afford optically active cyclic carbonates with kinetic resolution.[4] In this reaction, the di(ketoiminato)cobalt catalyst selectively activates one of the epoxide enantiomers by coordination of its oxygen atom to the metal center. This type of specific Lewis acid catalyst could be applied to several other catalyses, for example, hetero Diels–Alder reactions,[5] carbonyl–ene reactions,[6] and 1,3-dipolar cycloadditions of nitrones.[7] Based on a DFT study of a model system for the hetero Diels–Alder reaction, it was proposed that the specific catalytic activity of the di(ketoiminato)cobalt(III) complexes might be attributed to enhancement of the Lewis acidity as a consequence of the spin transition caused by coordination of a Lewis base to the metal center.[8]

On the other hand, the alternating copolymerization reaction of alkylene oxides, e.g., propylene oxide, and CO_2 producing poly(alkylene carbonate)s was developed by Inoue using a heterogeneous catalyst system derived from a 1:1 mixture of diethyl zinc and H_2O.[9] More efficient catalyst systems for this significant reaction have been proposed by our co-workers[10] and other groups[11] using cobalt–salen-type complex catalysts[12] (Scheme 1), which improved the selectivity of the carbonate linkages over the ether linkages in the obtained polymer. In this report, we describe the application of di(ketoiminato)cobalt complexes as a new class of Lewis acid catalysts for the alternating copolymerization of alkylene oxide and carbon dioxide and that these complexes exhibited not only good catalytic activity for the polycarbonate synthesis, but also an excellent selectivity for the formation of carbonate linkages without any ether linkage in the reactions of several alkylene oxides, especially for ethylene oxide (EO). In addition we would like to report the characteristic thermal decomposition behavior of the polycarbonate obtained in the present catalyst system.



Scheme 1. Alternating copolymerization of alkylene oxide and CO_2.

Table 1. Optimization of reaction temperature and counter anions with complex **1**[a]



Entry	Cobalt cat. 1 (X)	T /°C	Time /h	Polymer /%[b]	PPC /%[c]	Yield /%[d]	M_n /kg mol^{-1} [e]	M_w/M_n
1	**1a** (I)	30	12	43	>99	16	5.3	1.09
2	**1a** (I)	80	1	7	—	—	—	—
3	**1b** (OBz)	30	12	>99	>99	48	15.8	1.18
4	**1c** ($OBzF_5$)	30	12	99	>99	38	12.9	1.13

[a]The reaction was performed with 2.0 mL (28.6 mmol) of PO (**2a**) in the presence of **1** (14.3 µmol) and PPNCl (8.2 mg, 14.3 µmol) under 2.0 MPa of CO_2 atmosphere in an autoclave (30 mL). [b]The ratio of PPC/(PPC + PC) × 100. [c]The ratio of PPC/(PPC + PPO) × 100. [d]Isolated yield by precipitation from $CHCl_3$/MeOH. [e]Determined by gel permeation chromatography in tetrahydrofuran at 40 °C, calibrated with polystyrene standards.

First, a counter anion (X) on the cobalt center was examined using ethylene-bridged di(ketoiminato)cobalt(III) complexes **1a**–**1c** for the copolymerization of propylene oxide (PO) (**2a**) and CO_2 (Table 1). The reaction was performed in the presence of 0.05 mol % of the cobalt(III) complex **1** and bis(triphenylphosphoranylidene)ammonium chloride (PPNCl)[13] in a 1:1 ratio as catalysts using 2.0 mL of PO under 2.0 MPa of CO_2 pressure in an autoclave at 30 °C. After 12 h, the CO_2 pressure was slowly released. The crude material was analyzed by ^{1}H NMR, diluted with chloroform, quenched with methanolic HCl, precipitated by pouring it into an excess volume of methanol, and then dried in vacuo to isolate poly(propylene carbonate) (PPC). In the presence of the catalyst **1a** containing an iodide (X = I), the

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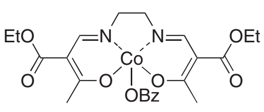
Table 2. Optimization of the ligand backbone[a]

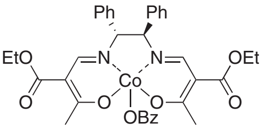
$$\text{PO } (\mathbf{2a}) + \text{CO}_2 \xrightarrow[\text{PPNCl (0.05 mol\%)} \atop 30\ ^\circ\text{C, 12 h}]{\text{catalyst (0.05 mol\%)}} \text{PPC } (\mathbf{3a}) + \text{PPO } (\mathbf{4a}) + \text{PC } (\mathbf{5a})$$

Entry	Catalyst	Yield /%[b]	Polymer /%[c]	PPC /%[d]	TOF /h^{-1} [e]	M_n /kg mol^{-1} [f]	M_w/M_n
1	**1b**	48	>99	>99	80	15.8	1.18
2	**6**	54	>99	98	90	18.0	1.13
3	**7**	47	>99	97	78	12.9	1.18
4	**8**	56	>99	>99	93	16.3	1.09
5	**9**	27	>99	>99	45	12.4	1.10
6	**10**	42	>99	>99	70	14.3	1.12
7	**11**	56	>99	>99	93	20.5	1.13

[a]The reaction was performed with 2.0 mL (28.6 mmol) of PO (**2a**) in the presence of the cobalt catalyst (14.3 µmol) and PPNCl (8.2 mg, 14.3 µmol) under 2.0 MPa of CO_2 atmosphere at 30 °C for 12 h in an autoclave (30 mL). [b]Isolated yield by precipitation from $CHCl_3$/MeOH. [c]The ratio of PPC/(PPC + PC) × 100. [d]The ratio of PPC/(PPC + PPO) × 100. [e]Turnover frequency of PO to PPC. [f]Determined by GPC/THF at 40 °C, calibrated with polystyrene standards.



1b



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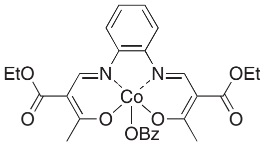

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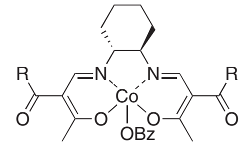
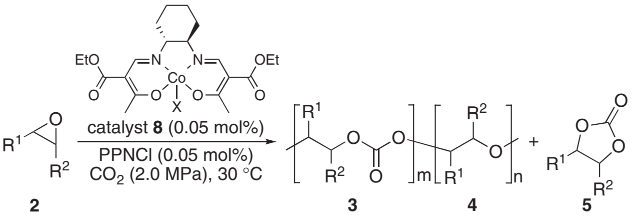
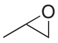
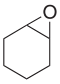
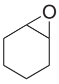
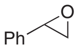


8-11

8 (R = OEt)
9 (R = Me)
10 (R = O^{i}Pr)
11 (R = O^{t}Bu)

Table 3. Various alkylene oxides[a]



Entry	Alkylene Oxide **2**		Cat. **8** (X)	Time /h	Yield /%[b]	**3/4/5**[c]	M_n[d] /kg mol^{-1}	M_w/M_n
1	**2a**		**8b** (OBz)	12	75	>99/0/<1	16.3	1.09
2	**2b**		**8a** (I)	48	29	48/0/52	8.7	1.20
3	**2b**		**8c** ($OBzF_5$)	48	26	95/0/5	37.1	1.33
4	**2c**[e]		**8a** (I)	48	70	>99/0/<1	4.3	1.10
5	**2c**[e]		**8c** ($OBzF_5$)	48	69	>99/0/<1	6.0	1.10
6	**2d**		**8c** ($OBzF_5$)	222	0	0/0/100	—	—

[a]The reaction was performed with alkylene oxide **2** (28.6 mmol) in the presence of cobalt catalyst **8** (14.3 µmol) and PPNCl (8.2 mg, 14.3 µmol) under 2.0 MPa of CO_2 atmosphere at 30 °C in an autoclave (30 mL). [b]Isolated yield by precipitation from $CHCl_3$/MeOH. [c]The ratio of polycarbonate/ether linkages/cyclic carbonate was determined by ^{1}H NMR. [d]Determined by GPC/THF at 40 °C, calibrated with polystyrene standards. [e]The reaction was performed in the presence of **8** (28.6 µmol) and PPNCl (16.4 mg, 28.6 µmol) in toluene (0.5 mL).

reaction proceeded to form the desired poly(propylene carbonate) (PPC) (**3a**) in 16% yield along with cyclic propylene carbonate (PC) (**5a**) in a ratio of 43:57, and the total conversion of the reaction was 62% (Entry 1). The reaction was performed at 80 °C in anticipation of a reaction acceleration, but the selectivity toward the polycarbonate **3a** unfortunately decreased (Entry 2). Alternatively, in order to improve the reactivity and/or selectivity, the cobalt(III) species **1b** and **1c** were examined. It was found that the complexes with $^-$OBz (**1b**, benzoate) or $^-$OBzF$_5$ (**1c**, pentafluorobenzoate) counter anion[14] gave a significantly improved selectivity in the reaction (Entries 3 and 4).

For further improvement of the reactivity and/or selectivity of the reaction, the ligand backbone of the cobalt(III) complexes was examined. With benzoate ($^-$OBz) as a counter anion, all four complexes **1b** and **6**–**8b** examined in this study exhibited an excellent PPC/PC selectivity of over 99% and the formation of carbonate **5a** was largely suppressed in each case (Table 2, Entries 1–4). Among these catalysts, the one with the *racemic trans*-1,2-cyclohexanediimine backbone (**8b**) gave the best result in terms of the balance of the reactivity and the selectivity (Entry 4). The complexes with *trans*-1,2-diphenylethylenediimine (**6**) and 1,2-phenylenediimine (**7**) showed comparable reactivity to catalyst **8b**, though they produced the polycarbonate **3a** containing ca. 2–3% of the ether linkages (**4a**) (Entries 2 and 3). The side-chain of the complexes was also examined (Entries 4–7). The complex with acetyl side-chains (**9**) exhibited an acceptable selectivity, but it was less reactive (Entry 5). The larger alkoxycarbonyl groups (**10** and **11**) did not show any better reactivity (Entries 6 and 7). Thus, we concluded that the complex **8b** was the best catalyst for the reaction, and applied these optimized reaction conditions to other epoxides (Table 3).

Under the same conditions for the PO/CO_2 copolymerization in Table 2, the reaction of ethylene oxide (EO, **2b**) (Table 3, Entries 2 and 3) or cyclohexene oxide (CHO, **2c**) (Entries 4 and 5) with CO_2 proceeded in the presence of the complex **8** to give the corresponding polycarbonates **3b** and **3c**, respectively. Especially, in the case of EO, a ^{1}H NMR analysis of the obtained polymer revealed that the catalyst system afforded the completely-alternating poly(ethylene carbonate) **3b** containing no ether linkage (**4b**). The characteristic peak corresponding to the carbonate (4.38 ppm) was observed as the only major peak, while that for the ether linkage (3.73 ppm) was negligible.[15]

It should be noted that the synthesis of the completely-alternating poly(ethylene carbonate) (PEC) from EO and CO_2 has been rarely accomplished,[16,17] and that the obtained polycarbonate is expected to have unique properties, e.g., thermal degradation behavior.

TG analyses were performed at the rate of 10 °C min^{-1} using 10 mg of the polycarbonate samples (Figure 1). For the commercially available PEC[18] containing ca. 5% ether linkages,

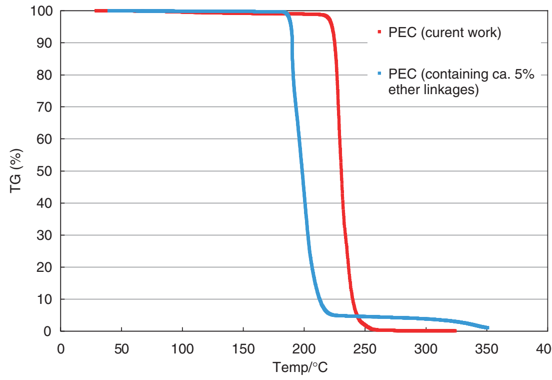


Figure 1. TG analyses of the poly(ethylene carbonate)s.

decomposition started at 190 °C,[19] but even at 220 °C approximately 5% of the weight still remained (blue line). The residue was not completely decomposed below 350 °C. In contrast, the polymer obtained in the current catalyst system started rapid decomposition at 220 °C,[19] and then completely decomposed below 260 °C without any residual weight (red line). It is assumed that this observed characteristic thermal degradation behavior is attributed to the structural regularity of the completely-alternating polymer structure, and this property will make it useful for applications such as evaporative pattern casting, ceramic binders, and adhesives.[20]

In summary, the di(ketoiminato)cobalt(III) complexes were successfully employed as a new class of catalysts for preparing poly(alkylene carbonate)s from alkylene oxide and CO_2. Consequently, a completely-alternating copolymer with ethylene oxide was obtained. It was confirmed that the obtained poly(ethylene carbonate) was completely decomposed within a narrow temperature range due to the completely-alternating carbonate linkages containing no ether linkage. Improvement of the catalytic activity of the present systems and investigation of the reaction mechanisms are ongoing studies.

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