Catalytic Reactions Involving C$_1$ Feedstocks: New High-Activity Zn(II)-Based Catalysts for the Alternating Copolymerization of Carbon Dioxide and Epoxides

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Carbon dioxide is an ideal synthetic feedstock since it is abundant, inexpensive, nontoxic, and nonflammable. Although it is estimated that Nature uses CO$_2$ to make over 200 billion tons of glucose by photosynthesis each year,[1] synthetic chemists have had little success in developing efficient catalytic processes that exploit this attractive raw material.[2] There has been considerable recent interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides to produce aliphatic polycarbonates.[3] Because of the low cost and accessibility of the monomers and the attractive properties of polycarbonates, the development of new, efficient initiators for this polymerization process is a significant scientific goal.[4−10] We report here a new class of well-defined, high-activity Zn(II) catalysts that copolymerize carbon dioxide and epoxides under exceptionally mild conditions.

The proposed mechanism of the copolymerization reaction is depicted in Scheme 1.[11] Repetition of the sequence in which CO$_2$ inserts into a metal alkoxide, followed by epoxide ring-opening with the metal carbonate forms the alternating copolymer. Two catalytic systems have been recently discovered that, prior to the present work, were the most active reported zinc-based systems for CO$_2$/epoxide polymerization. Darensbourg and Holtcamp have reported novel Zn(II) bis(2,6-diphenylphenoxide) initiators for the copolymerization of CO$_2$ and epoxides.[12] Immediately after initiation, it is probable that the remaining bulky phenoxide ligand of the complex prevents aggregation yet allows monomer coordination. Beckman et al. have developed a highly active Zn-based compound for cyclohexene oxide (CHO) copolymerization in supercritical CO$_2$.[13,14] The key to success in this system was a

Scheme 1
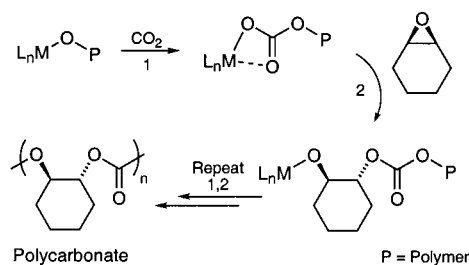
Scheme 2
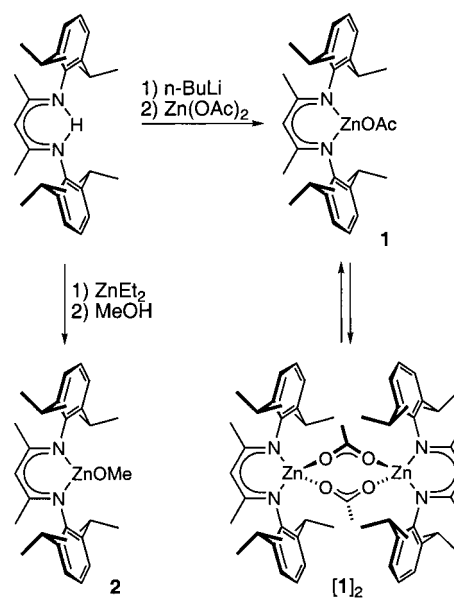
fluorinated carboxylate ligand that provided catalyst solubility in supercritical CO$_2$. In each of these systems, it is vital that the monomer does not displace the ligand from the active site during the polymerization reaction. On the basis of this lead, we investigated the synthesis and application of Zn(II) complexes incorporating chelating, bulky β-diimine ligands[15] as catalysts for epoxide/CO$_2$ copolymerization.

Deprotonation of the β-diimine ligand (BDI-H, derived from 2,6-diisopropylaniline)[16] with *n*-butyllithium and subsequent reaction with zinc acetate yields [(BDI)ZnOAc] (**1**) (Scheme 2).[17] Reaction of BDI-H with ZnEt$_2$ gives [(BDI)ZnEt], which produces [(BDI)ZnOMe] (**2**) upon reaction with methanol. The X-ray crystal structure of **1**[18] is shown in Figure 1; the structure reveals a tetrahedral zinc center and aryl groups that are approximately perpendicular to the plane of the N−Zn−N chelate. Complex **1** exists as the acetate-bridged dimer in the solid-state. The ^{1}H NMR spectrum of **1** in benzene-*d$_6$* (1 × 10^{-2} M) exhibits two sets of shifts whose intensities vary with concentration; the set that becomes more intense as concentration decreases was assigned

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Table 1. Results of Cyclohexene Oxide/CO_2 Polymerization by Zinc Compounds **1**−**4**[a]

catalyst	temp (°C)	pressure (psig)	reaction length (h)	% carbonate linkages	M_n (×10⁻³) (GPC)	M_w/M_n (GPC)	TON[b]	TOF[c] (h⁻¹)
1	20	100	2	95	21.3	1.07	270	135
1	50	100	2	96	31.0	1.11	494	247
1	80	100	2	95	25.7	1.17	412	206
2	50	100	2	95	19.1	1.07	449	224
3[d]	80	800	69	91	38.0	4.5	173	2.5
4[e]	100	2000	24	93	17.0	6.4	216	9.0

[a] All of the reactions were performed in neat CHO. [b] Moles of CHO consumed per mole of zinc. [c] Moles of CHO consumed per mole of zinc per hour. [d] Data from ref 12 for $(2,6-Ph_2C_6H_3O)_2Zn(Et_2O)_2$ (**3**). [e] Data from ref 13 for $HO_2CCH=CHCO_2(CH_2)_2C_6F_{13}/ZnO$ (**4**).
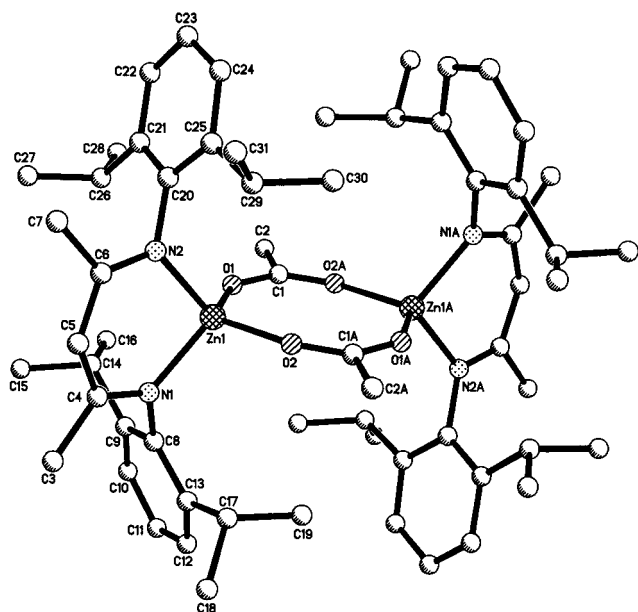

Figure 1. X-ray crystal structure of the dimer of **1**. Selected bond distances (Å) and angles (deg): Zn(1)−N(1), 1.970(2); Zn(1)−N(2), 1.969(2); Zn(1)−O(1), 1.946(2); Zn(1)−O(2), 1.965(2); C(1)−O(1), 1.239(3); C(1)−O(2A), 1.227(3); N(1)−Zn(1)−N(2), 98.48(8); O(1)−Zn(1)−O(2), 117.27(9); O(1)−Zn(1)−N(1), 112.33(8); O(2)−Zn(1)−N(2), 107.92(9); Zn(1)−O(1)−C(1), 138.3(2); O(1)−C(1)−O(2A), 128.4(3).

to the monomeric species. Thus, K_{eq} for the $2 \cdot \mathbf{1} \rightleftharpoons [\mathbf{1}]_2$ equilibrium is 34 M⁻¹ (C_6D_6 at 20 °C). In tetrahydrofuran-d_8 solution (1×10^{-2} M) only one set of shifts is present, which we have tentatively assigned to the monomeric species. Complexes **1** and **2** provide excellent model compounds for the putative metal carbonate and alkoxide intermediates of the polymerization reaction (Scheme 1).

Compounds **1** and **2** are virtually inactive for the homopolymerization of CHO (50 °C, 2h).[19] However the addition of low pressures of CO_2 gas to neat solutions of **1** or **2** in the epoxide monomer rapidly produces the polycarbonate. Data for the copolymerization of CHO and CO_2 with **1** and **2** are summarized in Table 1 (data for initiators $[(2,6-Ph_2C_6H_3O)_2Zn(Et_2O)_2]$ (**3**)[12] and $HO_2CCH=CHCO_2(CH_2)_2C_6F_{13}/ZnO$ (**4**)[13] are included for comparison). All four catalysts form polymers containing *trans*-rings and predominately carbonate linkages.[20] However complexes **1** and **2** operate under substantially milder conditions; even at moderate reaction temperatures (20−80 °C) and low CO_2 pressures (100 psig), the compounds are the most active reported catalysts for CHO/CO_2 copolymerization. Furthermore, the polymers produced are of high molecular weight and exhibit very narrow polydispersities, consistent with a living polymerization process. Compounds **1** and **2** under the same reaction conditions (50 °C, 100 psig) exhibit nearly identical activities, consistent with the proposal that alkoxide and carbonate intermediates are produced during the reaction.

In summary, we have discovered a new class of well-defined, highly active catalysts for the synthesis of highly alternated, high molecular weight, and monodispersed carbon dioxide/epoxide copolymers. Future work will explore the mechanism and modification of the current system to develop new generations of catalysts that exhibit higher activities or stereochemical control during the polymerization reaction.

Supporting Information Available: Syntheses of **1** and **2**, polymerization procedures, and crystal structure data for **1** (tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(17) (BDI)ZnOAc (**1**). To a solution of BDI-H (0.535 g, 1.28 mmol) in THF (10 mL) was slowly added *n*-BuLi (1.6 M in hexane, 0.88 mL, 1.41 mmol) at 0 °C. After stirring for 5 min at 0 °C, the solution was cannulated to a solution of zinc acetate (0.240 g, 1.31 mmol) in THF (15 mL). After stirring overnight at RT, the suspension was filtered over a frit, and the clear solution was dried in vacuo. The light yellow solid was recrystallized from a minimum amount of methylene chloride at −20 °C (0.436 g, 63% yield). ¹H NMR (25 mg complex in 0.55 mL C_6D_6, 300 MHz, M denotes monomer, D denotes dimer) δ 7.11 (18H, m, ArH, M + D), 4.93 (1H, s, β-CH, M), 4.64 (2H, s, β-CH, D), 3.29 (12H, m, C*H*Me₂, M + D), 1.73 (6H, s, OC(O)Me, D), 1.67 (6H, s, α-Me, M), 1.55 (12H, s, α-Me, D), 1.41 (12H, d, J = 6.4 Hz, CH*Me*Me′, M), 1.31 (3H, s, OC(O)Me, M), 1.19 (24H, d, J = 7.0 Hz, CH*Me*Me′, D), 1.14 (24H, d, J = 7.0 Hz, CHMe*Me*′, D), 0.87 (12H, d, J = 6.4 Hz, CHMe*Me*′, M).

(18) Crystal data of **1**: monoclinic, $P2_1/n$, colorless; a = 13.0558(3) Å, b = 15.1725(4) Å, c = 15.9712(2) Å; β = 106.142(1); V = 3038.99(11); Z = 4; R = 0.0535; GOF = 1.121.

(19) Compound **1** is, however, active for the homopolymerization of lactones such as ϵ-caprolactone. Cheng, M.; Coates, G. W., unpublished results.

(20) Polymers formed using **1** and **2** were subjected to basic hydrolysis. Analysis of the 1,2-cyclohexenediol degradation product by GC revealed that the diol was greater than 99% trans in configuration, consistent with inversion of stereochemistry during epoxide ring-opening. Consecutive epoxide insertion produces polymers that contain ether linkages.