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High-Activity, Single-Site Catalysts for the Alternating Copolymerization of CO_2 and Propylene Oxide

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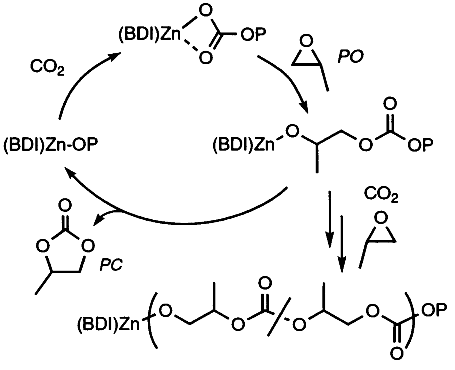
Because CO_2 is a nontoxic, nonflammable, and inexpensive substance, there is continued interest in its activation with transition-metal complexes and its subsequent use as a viable C1 feedstock.[1,2] One area that has seen considerable recent success is copolymerization of CO_2 and epoxides.[3]

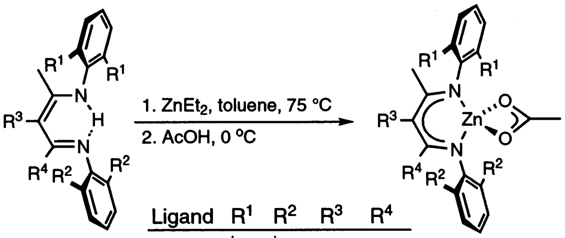
Several efficient catalyst systems for the copolymerization of CO_2 and cyclohexene oxide (CHO) have been recently reported.[3−9] *Interestingly, these catalysts do not readily polymerize related epoxides, such as propylene oxide (PO), with CO_2.* Inoue first showed that partially hydrolyzed $ZnEt_2$ initiated the copolymerization of PO and CO_2.[10,11] Since this discovery, a wide variety of initiating systems have been developed by mixing zinc sources (e.g., ZnO) with diprotic activators (e.g., glutaric acid).[3] The resultant systems, such as zinc glutarate, are structurally complex, insoluble mixtures. High catalyst loadings, elevated CO_2 pressures, and long reaction times must be employed to obtain appreciable amounts of polymer, which are often not perfectly alternating and exhibit broad molecular weight distributions. Currently, the preferred catalyst for PO/CO_2 copolymerization, zinc glutarate, exhibits activities as high as 4 turnovers of propylene oxide/CO_2 per mole of zinc per hour.[12,13] Because of the complex nature of this heterogeneous system, the active catalytic species are unknown; thus, rational modification of the catalyst is difficult. Discrete molecular catalysts provide an excellent opportunity to understand the mechanism of catalysis and to produce polymers with defined architectures.[14]

Part of the difficulty in developing well-defined PO/CO_2 polymerization catalysts results from the complexity of the copolymerization cycle. In a model copolymerization, the enchainment steps of both CO_2 and PO would have low activation barriers and similar negative $\Delta G°$ values. Moreover, pathways to cyclic carbonates[15] would be inaccessible (Scheme 1). Despite the ring-strain of epoxides, the rate-determining step of CHO/CO_2 polymerizations using β-diiminate (BDI) zinc complexes such as [(BDI-**1**)ZnOAc] involves CHO enchainment. Unexpectedly, CO_2 enchainment is rapid and not generally rate-limiting. We attribute the facile CO_2 enchainment step to a weakly coordinated monomeric zinc alkoxide [(BDI-**1**)ZnOR] being converted to a stable four-coordinate zinc carbonate [(BDI-**1**)Zn(η^2-OCO_2R)]. If this is indeed the case, ligand modifications that alter the coordination state of the alkoxide would be expected to cause significant changes in polymerization activity. With studies underway to determine the precise energetics of these copolymerizations, we embarked on empirical modifications of the complexes to discover improved catalysts. Herein we communicate our progress in the development of homogeneous catalysts for the copolymerization of PO and CO_2.

Scheme 1. Copolymerization Scheme (P = Polymer Chain)



Scheme 2. Synthesis of [(BDI)ZnOAc] Complexes



Ligand	R^1	R^2	R^3	R^4
BDI-1	^{i}Pr	^{i}Pr	H	CH_3
BDI-2	^{i}Pr	Et	CN	CH_3
BDI-3	^{i}Pr	Et	H	CF_3
BDI-4	Et	^{i}Pr	H	CF_3
BDI-5	Et	^{i}Pr	CN	CF_3

Although [(BDI-**1**)ZnOAc] rapidly polymerizes CHO and CO_2, it only produces traces of cyclic material and virtually no polymer from PO and CO_2 (Table 1, entry 2).[16] We have recently reported that unsymmetrical β-diiminate zinc initiators bearing electron-withdrawing groups show unprecedented activities for the copolymerization of CHO and CO_2.[9] Screening these catalysts for PO/CO_2 activity revealed that [(BDI-**2**)ZnOAc] produces propylene carbonate (PC) at 50 °C (Table 1, entry 3). Simply reducing the temperature from 50 to 25 °C (Table 1, entry 4) suppressed the formation of PC and allowed for the synthesis of poly(propylene carbonate) (PPC) with 85% selectivity.[17] To our surprise, complexes with symmetrical ligands (R^1, R^2 are all Et or ^{i}Pr) are inactive for either PC or PPC formation. Based on the success of unsymmetrical, electron-deficient [(BDI-**2**)ZnOAc], we synthesized related complexes with electron-withdrawing substituents and different aryl groups on the BDI ligand (Scheme 2). Reaction of $ZnEt_2$ with the BDI ligand followed by addition of HOAc at 0 °C yields the crystalline [(BDI)ZnOAc] complexes in 38−65% yield. Slow cooling of a concentrated toluene solution of the resulting complexes gives X-ray quality crystals. The molecular structures of [(BDI-**3**)ZnOAc], [(BDI-**4**)ZnOAc], and [(BDI-**5**)ZnOAc] are similar to other [(BDI)ZnOAc] complexes previously reported.[7,8,18] The compounds are acetate bridged dimers in the solid state, with distorted tetrahedral zinc centers separated by ~4.2 Å. The

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Table 1. Propylene Oxide/CO_2 Copolymerization Results[a]

entry	catalyst	time (h)	temp (°C)	pressure (psi)	TOF[b] (mol PO/(mol Zn·h))	selectivity[c] PPC:PC	M_n ($\times 10^{-3}$)[d]	PDI (M_w/M_n)
1[e]	Zn-glutarate	40	50	758	3.4	NR[f]	143	2.4
2	[(BDI-**1**)ZnOAc]	8	25	300	3	<1:100	NA[g]	NA[g]
3	[(BDI-**2**)ZnOAc]	8	50	300	50	<1:100	NA[g]	NA[g]
4	[(BDI-**2**)ZnOAc]	8	25	300	47	85:15	43.3	1.09
5	[(BDI-**3**)ZnOAc]	8	25	300	26	72:28	21.9	1.10
6	[(BDI-**4**)ZnOAc]	2	25	300	212	87:13	35.9	1.11
7	[(BDI-**5**)ZnOAc]	8	25	300	0	NA[g]	NA[g]	NA[g]
8	[(BDI-**4**)ZnOAc]	2	25	100	235	75:25	36.7	1.13
9	[(BDI-**4**)ZnOAc]	2	25	500	138	93:7	30.6	1.15
10	[(BDI-**4**)ZnOAc]	2	40	300	215	20:80	16.6	1.27
11	[(BDI-**4**)ZnOAc]	2	10	300	37	93:7	10.0	1.16

[a] All of the polymerizations were carried out in neat PO (4.9 mL) with [monomer]/[Zn] = 2000 unless otherwise noted. [b] Turnover frequency of PO to products. [c] Based on the ^{1}H NMR integration of PPC and PC resonances at the end of the reaction. [d] Determined by gel permeation chromatography relative to polystyrene standards in tetrahydrofuran. [e] Reference 12. [f] Not reported. [g] Not applicable.

complexes crystallize to alleviate steric repulsions, positioning the isopropyl substituted aryl groups anti to each other.

Subtle changes in the ligand architecture drastically affect the catalyst activity for PPC formation (Table 1, entries 4−7).[19] Shifting the CF_3 group from the side of the diethyl aniline to the side of the diisopropyl aniline yields a nearly 10-fold increase in activity. On the other hand, placing both a CN group and a CF_3 group on the backbone of the ligand results in complete deactivation of the complex, yielding neither polymer nor cyclic carbonate. The intriguing sensitivity of this reaction to steric and electronic perturbations of the BDI ligand is currently being studied and further exploited.

As anticipated, varying the reaction temperature and CO_2 pressure affects both the selectivity and the activity of the superior catalyst, [(BDI-**4**)ZnOAc]. As seen in entries 6, 8, and 9, increasing the pressure of CO_2 from 100 to 500 psi suppresses cyclic carbonate formation, increasing the selectivity for polymer from 75 to 93% while moderately decreasing the catalyst activity for PPC formation. This suggests that PC is formed by a backbiting reaction of the metal alkoxide intermediate (Scheme 1). Entries 6, 10, and 11 show that lowering the reaction temperature dramatically increases selectivity for polymer formation, although catalyst activity for PPC formation is optimum at 25 °C.

All of the isolated polymers have narrow polydispersity indices and M_n values close to the predicted values, hallmarks of living polymerizations. The ^{1}H NMR spectra of all PPCs produced show >99% carbonate linkages, and the ^{13}C NMR spectra of the PPCs show head/head, tail/tail, and head/tail linkages in the ratio 23:23:54. Such a microstructure is consistent with a near regiorandom ring-opening of PO and is similar to polymers made using zinc glutarate (∼60% head/tail linkages).[20] Notably, the T_g of the polymer (38 °C) is the same as that for PPC made using zinc glutarate.[12]

In conclusion, we report several [(BDI)ZnOAc] complexes that are active for PO/CO_2 copolymerization. The activity observed for [(BDI-**4**)ZnOAc] is significantly higher than any other reported catalyst. The alternating polymers produced are regioirregular and exhibit narrow molecular weight distributions. Future efforts are directed toward understanding the mechanism of catalysis and controlling the regio- and stereochemistry of the copolymerization.

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Supporting Information Available: Synthesis and characterization of complexes and polymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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