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Alternating Copolymerization of CO_2 and Propylene Oxide Catalyzed by Co^{III}(salen)/Lewis Base

Robert L. Paddock and SonBinh T. Nguyen*

Department of Chemistry and Institute for Environmental Catalysis, Northwestern University, 2145 Sheridan Rd., Evanston, Illinois 60208

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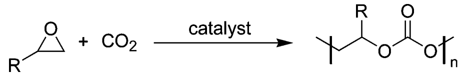
CO_2 is naturally abundant, nontoxic, nonflammable, inexpensive, and easy to store, transport, and handle, making it an attractive alternative C_1 feedstock. Unfortunately, despite a substantial amount of effort, few efficient and economical synthetic processes have been developed which utilize CO_2 as a reagent.[1] One of the most promising methodologies being investigated in this area, so-called chemical CO_2 fixation, is the alternating copolymerization of CO_2 and epoxides (eq 1).[2−4] This reaction was first reported by Inoue and co-workers in 1969, employing a heterogeneous catalyst synthesized from $ZnEt_2$ and water.[5] In the years following this initial report, a variety of heterogeneous catalyst systems have been developed with limited success, generally suffering from irreproducibility, low activity, high polyether content in the polycarbonate product, and production of significant amounts of the undesired cyclic carbonate byproduct. In the past decade, several well-defined single site catalysts have been reported which demonstrate greatly improved activity and selectivity for reaction 1.[6−16] These catalysts are especially active in the copolymerization of CO_2 and alicyclic epoxides such as cyclohexene oxide, which are sterically inhibited from producing the cyclic carbonate byproduct.[17] Unfortunately, these same catalysts are much less effective when aliphatic epoxides such as propylene oxide (PO) are employed as substrates; even those which are active generally suffer from concomitant production of cyclic carbonate.



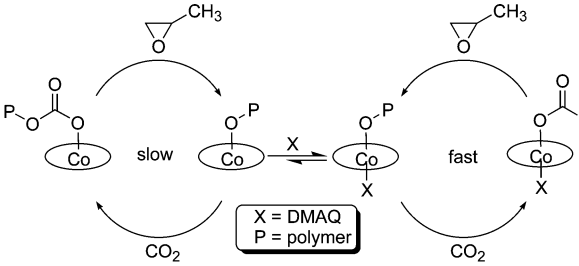
(1)

Recently, Coates et al. reported that Co^{III}(salen) complexes catalyze the copolymerization of CO_2 and propylene oxide to yield poly(propylene carbonate) (PPC) with an unprecedented selectivity (>99%) for the polycarbonate vs the cyclic carbonate product.[13] However, these catalysts were only active at very high CO_2 pressures with optimal reaction conditions requiring 800 psig of CO_2. Since 2001, our group has been investigating binary Lewis acid/Lewis base catalyst systems for the coupling reaction of CO_2 and three-member heterocycles,[18−21] and at the time of Coates report we were investigating Co^{III}(salen)/Lewis base catalyst systems for the synthesis of cyclic carbonates.[21] During the course of those investigations, we were very pleased to discover the formation of PPC can be induced to occur at low temperatures and low CO_2 pressure regimes where Coates et al. had reported that Co^{III}(salen) complexes by themselves are inactive. Herein, we report our results employing the Co^{III}(salen)/Lewis base catalyst system in the alternating copolymerization of CO_2 and PO.

Initially, enantiomerically pure (*R,R*)-Co^{III}(salen) complex **1a**, in conjunction with *N,N*-dimethylaminoquinoline (DMAQ), was investigated as a catalyst system for the copolymerization of PO and CO_2 over a wide range of CO_2 pressures (Table 1, entries 1−5). This catalyst system was found to be active at low CO_2 pressures, with optimal activity achieved in the range of 150−350 psig of CO_2.[22] It is even active at CO_2 pressures as low as 50 psig, maintaining over 50% of its optimal turnover frequency (TOF). Increasing the pressure above the optimal CO_2 pressure range resulted in a significant drop-off in reaction rate.

The generally accepted mechanism for the copolymerization of CO_2 and epoxides involves the alternate enchainment of CO_2 and the epoxide via insertion into either a metal alkoxide or carbonate bond (Scheme 1).

Scheme 1. Proposed Mechanism for the Copolymerization of CO_2 and PO



Recently, a number of elegant mechanistic studies have been conducted to determine the possible role of a Lewis base cocatalyst in the copolymerization of CO_2 and epoxides catalyzed by single site Cr and Al complexes.[14,23,24] These studies have suggested that the Lewis base coordinates to the active metal center trans to the propagating metal−polymer chain, thereby labilizing the metal alkoxide bond and facilitating the insertion of CO_2. We believe that DMAQ functions in an analogous manner in our catalyst system, dramatically increasing the rate of CO_2 enchainment, thereby explaining the high copolymerization activity at low CO_2 pressures for the Co^{III}(salen) complexes in the presence of the Lewis base.

The ratio of catalyst to Lewis base cocatalyst was also found to influence the TOF (Table 1, entries 2, 6−8). Optimal activity occurred when 2 equiv of cocatalyst was employed. Using only 1 equiv of DMAQ decreased the activity by over 50%, whereas an increase beyond 2 equiv lead to a slight decrease in activity along with a slight increase in the polymer dispersity. In general, **1a**/DMAQ was highly selective for the polycarbonate product (>99%), which was completely alternating, typically exhibiting >99% carbonate linkages. The polycarbonate products have very narrow polydispersity indices (PDI <1.1); however, the observed number-average molecular weight (M_n, vs polystyrene standards) was generally below the expected stoichiometric value, which has been suggested as being indicative of chain transfer during the reaction.[15]

The nature of the catalyst's counteranion and ligand structure were found to influence both the activity and stereoselectivity of the copolymerization. The TOF

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* Corresponding author: Fax 847-491-7713; Tel 847-467-3347; e-mail stn@northwestern.edu.

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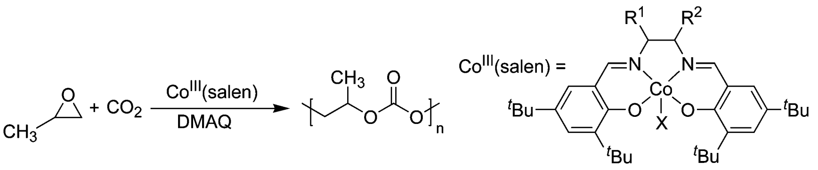
Table 1. CO_2/PO Copolymerization Results[a]



1a: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = OTs
1b: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = Cl
1c: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = OAc
1d: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = OTf
1e: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = BF_4
1f: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = I
1g: $R^1$and R^2 = (*R,R*)-*trans* -(CH_2)$_4$-, X = NO_3
2g: R^1 = (*R*)-CH_3, R^2 = H, X = NO_3
3g: (*R,R*)-*trans*, R^1 = R^2 = Ph, X = NO_3

entry	catalyst	press. (psig)	DMAQ (equiv)	temp (°C)	time (h)	TOF[b] (h^{-1})	selectivity[c] (% PPC)	carbonate linkages (%)[c]	M_n[d] (g mol^{-1})	PDI (M_w/M_n)	k_{rel}[e]
1	**1a**	50	2	rt	5	47	>99	>99	17.1	1.07	5.1
2	**1a**	150	2	rt	5	86	>99	>99	25.6	1.06	5.3
3	**1a**	350	2	rt	5	75	>99	>99	21.7	1.06	4.8
4	**1a**	500	2	rt	6	49	>99	>99	18.2	1.07	4.7
5	**1a**	750	2	rt	12.5	16	>99	>99	14.4	1.08	4.7
6	**1a**	150	1	rt	10	41	>99	>99	35.2	1.06	5.1
7	**1a**	150	3	rt	4.5	83	>99	>99	17.6	1.08	5.4
8	**1a**	150	5	rt	5	71	>99	>99	10.8	1.25	5.2
9	**1b**	150	2	rt	5	40	98	99	11.2	1.16	5.0
10	**1c**	150	2	rt	5	43	>99	>99	12.3	1.17	5.0
11	**1d**	150	2	rt	5	63	>99	>99	20.3	1.05	5.0
12	**1e**	150	2	rt	5	86	>99	>99	21.3	1.06	4.4
13	**1f**	150	2	rt	5	91	86	>99	23.5	1.07	4.2
14	**1g**	150	2	rt	5	97	>99	>99	23.2	1.07	5.1
15	**2g**	150	2	rt	3	118	>99	>99	17.2	1.06	2.0
16	**3g**	150	2	rt	3.25	118	>99	>99	17.8	1.06	1.2
17	**3g**	350	2	40	1.66	199	>99	>99	17.4	1.07	1.9
18	**3g**	350	2	60	1.5	145	92	>99	12.9	1.18	1.7
19	**3g**	350	2[f]	40	0.66	589	>99	>99	18.4	1.05	1.9

[a] Reaction conditions: catalyst (0.067 mol %, 3.33×10^{-5} mol), PO (1500 equiv, 3.5 mL). [b] Moles of product (polymer and cyclic carbonate) per mole of catalyst per hour. [c] Determined using ^{1}H NMR spectroscopy. Only side product is PC. [d] Determined by gel permeation chromatography at 35 °C relative to polystyrene standards. [e] $k_{rel} = \ln[1 - c(1 + ee)]/\ln[1 - c(1 - ee)]$, where c = conversion and ee = enantiomeric excess of unreacted PO.[28] [f] DMAP* was employed as the Lewis base cocatalyst.

changed with the identity of the counteranion (Table 1, entries 2, 9–14), with the NO_3^- anion providing the most active catalyst **1g**. However, there is no obvious trend in the relationship between counteranion identity and catalyst activity. For the same counteranion, changing the salen ligand framework to incorporate noncyclic backbones resulted in a slight improvement in TOF as well as a significant drop-off in stereoselectivity, as determined by the enantiomeric excess (ee) of the remaining PO (Table 1, entries 14–16). A k_{rel} of 5.1 is obtained with the (*R,R*)-cyclohexyl backbone, whereas the (*R,R*)-diphenyl and (*R*)-propyl backbones of catalyst **2g** and **3g** gave a k_{rel} of only 2.0 and 1.2, respectively. (In the absence of a cocatalyst, Coates et al. reported a k_{rel} of only 2.8 for Co^{III}(salen) complexes with a (*R,R*)-cyclohexyl backbone.[13]) We postulate that the improvement in enantioselectivity observed with the addition of the DMAQ cocatalyst may be a result of the steric interactions between the coordinated amine and the salen ligand framework. These interactions may lead to an "improved" ligand geometry about the active metal center that is better able to induce enantioselectivity during the reaction. In addition to an increase in enantioselectivity, the utilization of the DMAQ cocatalyst also lead to a considerable improvement in regioselectivity in regards to PO enchainment. Examination of the carbonate region of the ^{13}C NMR spectra of the polycarbonate product[25] resulting from the copolymerization of racemic PO and CO_2 shows that **1a**/DMAQ is highly regioselective, as the polycarbonate product exhibits a microstructure with a head-to-tail content of 96% (Figure 1). In comparison, Coates et al. obtained only 80% head-to-tail linkages for the copolymerization of racemic PO and CO_2 when employing Co^{III}(salen) complexes as catalysts in the absence of a Lewis base.[13]

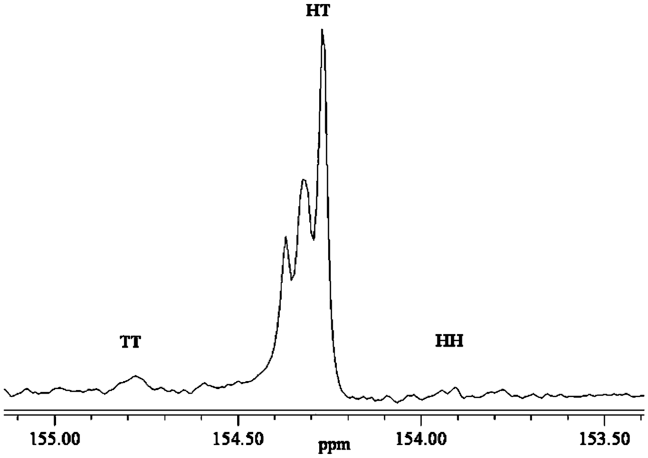


Figure 1. ^{13}C spectrum (100 MHz) of the carbonyl region for PPC obtained using catalyst **1a**/DMAQ.

Previous reports have demonstrated that increasing the reaction temperature for the alternating copolymerization of CO_2 and PO generally results in a decrease in selectivity for PPC as more cyclic carbonate is produced.[9,16,26] For **3g**/DMAQ, increasing the temperature to 40 °C only had the positive effect of improving the TOF and did not lead to production of the cyclic carbonate. An increase in temperature to 60 °C eventually led to slight decreases in TOF and selectivity for PPC, as 8% of the product mixture was propylene carbonate (Table 1, entries 15, 17–18).

In our prior investigations of the Co^{III}(salen)/Lewis base catalyst system for the synthesis of cyclic carbonates,[21] we discovered that employing (*R*)-(+)-4-(dimethylamino)pyrindinyl(pentaphenylcyclopentadienyl) iron (DMAP*) as a cocatalyst resulted in a higher TOF than that obtained with DMAQ, perhaps as a result of its increased Lewis basicity.[27] In our current studies we also observed the desired improvement in activity when utilizing DMAP*, obtaining a TOF of 589 h^{-1} at 40 °C (Table 1, entry 19), which to the best of our knowledge is the highest TOF reported to date for the alternating copolymerization of CO_2 and PO.

In summary, we have demonstrated that Co^{III}(salen)/Lewis base catalyst systems are highly active and selective in the copolymerization of CO_2 and propylene oxide. The use of the Lewis base cocatalyst enables high catalytic activity at low CO_2 pressures, affords superior regio- and enantioselectivity, and produces a highly alternating, monodisperse polycarbonate product without concomitant cyclic carbonate production. Future work will be directed toward obtaining mechanistic insight as well as further improvements of the activity and stereoselectivity via optimization of the catalyst and cocatalyst structure through perturbation of the steric and electronic parameters.

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Supporting Information Available: General experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953−996.

(2) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618−6639.

(3) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(4) Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919−992.

(5) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B* **1969**, *7*, 287−292.

(6) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577−7579.

(7) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368−372.

(8) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019.

(9) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487−12496.

(10) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303−308.

(11) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599−2602.

(12) Eberhardt, R.; Allendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194−196.

(13) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484−5487.

(14) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. *Acc. Chem. Res.* **2004**, *37*, 836−844.

(15) Lu, X. B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574−3577.

(16) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107−116.

(17) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586−7591.

(18) Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498−11499.

(19) Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**, *6*, 2301−2304.

(20) Paddock, R. L.; Hiyama, Y.; McKay, J. M.; Nguyen, S. T. *Tetrahedron Lett.* **2004**, *45*, 2023−2026.

(21) Paddock, R. L.; Nguyen, S. T. *Chem. Commun.* **2004**, *14*, 1622−1623.

(22) During the course of our work Lu et al. reported that a Co^{III}-(salen)/ammonium salt catalyst system is active for the alternating copolymerization of PO and CO_2 at low pressures; see ref 15.

(23) Chisholm, M. H.; Zhou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 11030−11039.

(24) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43*, 1831−1833.

(25) Chisholm, M. H.; DaVarro-Llobet, D.; Zhou, Z. *Macromolecules* **2002**, *35*, 6494−6504.

(26) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284−14285.

(27) Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412−420.

(28) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley and Sons: New York, 1994; pp 1267.

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