Polycarbonate Synthesis

Cobalt-Based Complexes for the Copolymerization of Propylene Oxide and CO_2: Active and Selective Catalysts for Polycarbonate Synthesis**

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CO_2 is an ideal feedstock for chemical synthesis as it is safe and abundant.[1] However its thermodynamic stability hinders its utility as a starting material in synthetic reactions. A topic of current interest is the development of catalysts that can exploit CO_2 by combining it with highly reactive reagents, thus resulting in thermodynamically and kinetically viable reactions. Perhaps the most promising reaction of this type is the alternating copolymerization of CO_2 with epoxides to aliphatic polycarbonates,[2] which was first reported by Inoue et al. in the late 1960's.[3] More recently, highly active discrete complexes have been discovered that offer significant advantages over traditional heterogeneous catalysts. Although noteworthy successes were realized for the copolymerization of CO_2 with alicyclic epoxides (such as cyclohexene oxide),[4–12] catalysts that exhibit high activities with aliphatic epoxides (such as propylene oxide, PO),[13–16] without the concomitant production of cyclic carbonates, have not been reported. Herein we report the use of cobalt-based catalysts that exhibit excellent activity and selectivity for the synthesis of poly(propylene carbonate) (PPC).

The generalized mechanism of CO_2/epoxide copolymerization involves two steps: 1) epoxide ring opening by a metal carbonate, followed by 2) CO_2 insertion into a metal alkoxide (Scheme 1). When aliphatic epoxides such as propylene oxide are used, a common side-product is the cyclic carbonate, likely formed by a back-biting reaction from the propagating alkoxide.[14] In fact, the most active PPC catalysts reported to date produce 10–30% of the unwanted cyclic propylene carbonate byproduct under optimized conditions.[14,16]

In our search for new polymerization catalysts, we focused our efforts on ligand/metal combinations known to effect both of the productive steps of polycarbonate formation. Although cobalt catalysts have essentially no precedent in CO_2/epoxide polymerization,[17] recent reports documented the utility of discrete cobalt complexes in each of the vital

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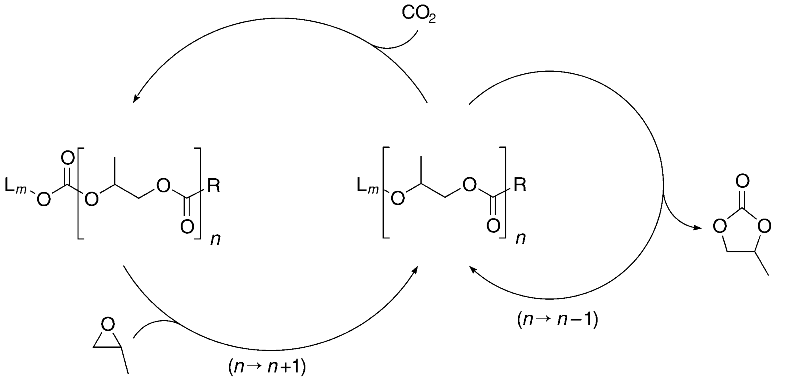
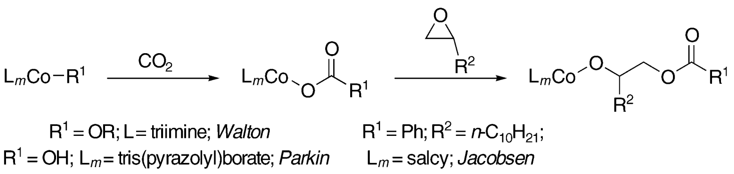


Scheme 1. Mechanism of CO_2/epoxide copolymerization by using discrete metal alkoxides (R = OR′) and carboxylates (R = alkyl, aryl).

steps of the copolymerization (Scheme 2).[18] Jacobsen and coworkers have recently shown that (salcy)Co^{III} carboxylates (salcy = *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) can efficiently ring-open epoxides,[19,20] whereas Co hydroxides[21,22] and alkoxides[23,24] have been documented



Scheme 2. Recent examples of reactions of cobalt complexes that suggest the potential utility of [L_mCoOR] complexes for epoxide/CO_2 copolymerization.

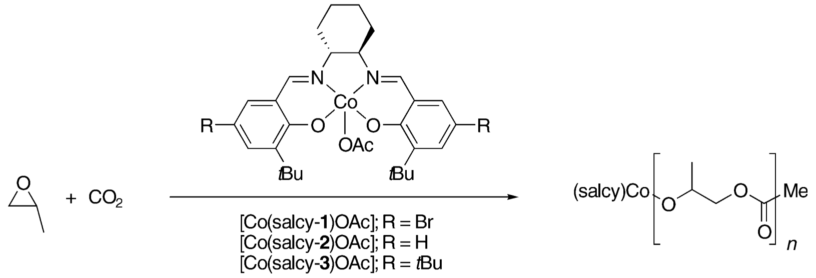
to form carbonates in the presence of CO_2. Furthermore, to suppress unwanted cyclic carbonate formation, we proposed that catalysts incapable of lactone polymerization might exhibit improved selectivities because of the mechanistic similarity between lactone enchainment and cyclic carbonate extrusion (Scheme 1). Interestingly, efficient cobalt complexes have not been reported for lactone polymerization, thus suggesting possible selectivity for polycarbonate formation.[25] We focused our initial efforts on Co^{III}(salcy) complexes given their spectacular performance in the hydrolytic kinetic resolution of aliphatic epoxides,[19,20] as well as the documented performance of their chromium counterparts for the synthesis of cyclic-[26] and polycarbonates.[12,15,16]

We initially investigated the use of various [Co(salcy)OAc] complexes for the polymerization of propylene oxide with CO_2 at low pressures, but found them to be inactive. Given the known reactivity of Co(salcy) carboxylates with epoxides,[19,20] we reasoned the problematic sequence in the reaction pathway was CO_2 insertion. Upon exploring reactions at higher pressures of CO_2, we discovered [Co(salcy)OAc] complexes were highly active and selective catalysts. Shown in Table 1 are the complexes used as well as their polymerization data. Catalysts [Zn(BDI)OAc][14] (BDI = β-diiminate) and [Cr(salph)Cl]/DMAP[16] (salph = bis(3,5-di-*tert*–butylsalicylidine)-1,2-phenylenediamine dianion; DMAP = dimethylaminopyridine) are included for comparison (entry 14, [Zn(BDI)OAc] and entry 15, [Cr(salph)Cl]/DMAP. All of the cobalt catalysts are enantiomerically pure (*R,R*-stereochemistry), thus enabling the stereoselectivity of epoxide enchainment to be measured (see below). The complex [Co(salcy–**1**)OAc] was used to study the effect of the reaction conditions on polymer formation. Entry 1 shows the CO_2 pressure and reaction temperature for optimal catalyst activity. [Co(salcy–**1**)OAc] requires high pressure (800 psi) for the most favorable activity, which is approximately half of that of the benchmark Zn and Cr catalysts. However, a notable advantage of [Co(salcy–**1**)OAc] is a much higher selectivity for polymer formation; the cyclic by-product propylene carbonate is not formed in measurable quantities. The resultant polycarbonates are highly alternated with 95 % carbonate linkages. Molecular weight distributions of the polycarbonates produced by [Co(salcy)OAc] complexes are generally narrow, consistent with a controlled polymerization, however values of $\bar{M}_n$ ($\bar{M}_n$ is the number-average molar mass) are about half those expected, [14] which we tentatively attribute to chain transfer to water or acetic acid molecules that were coordinated to the catalyst during synthesis.[19] Entry 2 shows the profound effect of lowering the CO_2 pressure; at 600 psi, the reaction rate is quartered and at lower pressures the catalyst is essentially inactive. Entries 3–6 show the strong influence of reaction temperature. Catalyst activity decreases at temperatures above and below 25 °C; ether linkages are notably present in higher content (10 %) at 40 °C. Entry 7 shows that propylene oxide conversion is acceptable (77 %) at higher catalyst loadings, while entry 8 shows that high-molecular-weight polymer can be formed at low catalyst loadings.

[Co(salcy–**2**)OAc] shows minor difference in catalytic properties versus [Co(salcy–**1**)OAc] (entries 9, 10), although [Co(salcy–**3**)OAc] with the sterically bulky *para tert*-butyl group shows notable differences (entries 11–13). Although the activities of [Co(salcy–**3**)OAc] are slightly lower than [Co(salcy–**1**)OAc], the polymers produced are almost perfectly alternating polycarbonates. As with the other [Co(salcy)OAc] complexes, cyclic propylene carbonate is not formed. Regarding the regioselectivity of propylene oxide enchainment,[27] [Co(salcy–**3**)OAc] is highly selective with 80 % head-to-tail linkages. In contrast, the catalysts [Co(salcy–**1**)OAc], [Co(salcy–**2**)OAc], and [Zn(BDI)OAc][14] have typical regioselectivities of 70, 75, and 60 %, respectively. Polymerization of (*S*)-propylene oxide with enantiomerically-pure [Co(salcy–**3**)OAc] (entry 13), yields an isotactic (*S*) polymer with an unprecedented head-to-tail content of 93 % was obtained. [Co(salcy–**3**)OAc] preferentially consumes (*S*)-propylene oxide over (*R*)-propylene oxide with a k_{rel} of 2.8 (entry 12); given the same absolute configuration and similar k_{rel} observed by Jacobsen in the ring-opening of aliphatic epoxides with benzoic acid,[19] we propose a related mechanism occurs in the polymerization to give the active alkoxide regiochemistry as shown in Table 1.

In summary, we report the first discrete cobalt complexes for the copolymerization of CO_2 and epoxides. In contrast to

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



Entry	Catalyst	Epoxide	[PO]:[Cat]	Pressure [psi]	Temp [°C]	Time [h]	TOF[b] [h^{-1}]	Selectivity (% PPC)[c]	Carbonate Linkages [%][c]	$\bar{M}_n$[d] [$g\,mol^{-1}$]	PDI ($\bar{M}_w/\bar{M}_n$)
1	[Co(salcy–**1**)OAc]	*rac*-PO	500	800	25	3	81	> 99	95	15300	1.22
2	[Co(salcy–**1**)OAc]	*rac*-PO	500	600	25	3	19	> 99	94	3100	2.60
3	[Co(salcy–**1**)OAc]	*rac*-PO	500	800	40	3	17	> 99	90	5600	1.21
4	[Co(salcy–**1**)OAc]	*rac*-PO	500	800	30	3	69	> 99	94	12200	1.26
5	[Co(salcy–**1**)OAc]	*rac*-PO	500	800	20	3	42	> 99	95	8000	1.44
6	[Co(salcy–**1**)OAc]	*rac*-PO	500	800	15	3	31	> 99	95	7600	1.51
7	[Co(salcy–**1**)OAc]	*rac*-PO	200	800	25	3	51	> 99	95	8200	1.25
8	[Co(salcy–**1**)OAc]	*rac*-PO	2000	800	25	8	38	> 99	95	21700	1.41
9	[Co(salcy–**2**)OAc]	*rac*-PO	200	800	25	3	51	> 99	96	6600	1.21
10	[Co(salcy–**2**)OAc]	*rac*-PO	500	800	25	3	66	> 99	96	9000	1.31
11	[Co(salcy–**3**)OAc]	*rac*-PO	200	800	25	3	42	> 99	99	5700	1.28
12	[Co(salcy–**3**)OAc]	*rac*-PO	500	800	25	3	59	> 99	99	8100	1.57
13	[Co(salcy–**3**)OAc]	*(S)*-PO	500	800	25	3	71	> 99	99	6900	1.58
14[e]	[Zn(BDI)OAc]	*rac*-PO	2000	300	25	2	184	87	99	35900	1.11
15[f]	[Cr(salph)Cl]	*rac*-PO	1500	490	75	4	160	71	98	16700	1.38

[a] All of the polymerizations were carried out in 3.5 mL of neat propylene oxide (PO). [b] Turnover frequency of PO to PPC. [c] Determined by using ^1H NMR spectroscopy. [d] Determined by gel permeation chromatography in tetrahydrofuran at 40 °C, calibrated with polystyrene standards. [e] Reference [14]. [f] Reference [16].

the chromium catalysts, [Co(salcy)OAc] complexes do not require heterocyclic additives for optimal catalytic activity. Although [Co(salcy)OAc] catalysts are only half as active as highly active Cr and Zn catalysts, they have notable advantages such as high selectivity to polymer as well as excellent regioselectivity. In addition, [Co(salcy)OAc] catalysts are remarkably robust, thus allowing the use of unpurified monomers and bench-top reaction setup. Our future efforts are directed toward the study of the reaction mechanism, as well as development of catalysts that exhibit higher stereoselectivities for epoxide ring-opening.

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