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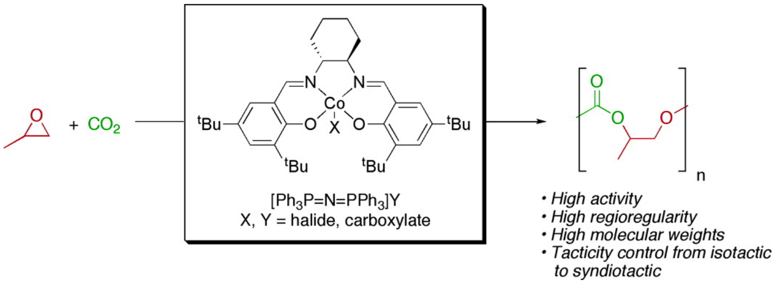
J. Am. Chem. Soc., **2005**, 127 (31), 10869-10878• DOI: 10.1021/ja051744l • Publication Date (Web): 14 July 2005



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Cobalt Catalysts for the Alternating Copolymerization of Propylene Oxide and Carbon Dioxide: Combining High Activity and Selectivity

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Abstract: Synthetic pathways to (salcy)CoX (salcy = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane; X = halide or carboxylate) complexes are described. Complexes (*R*,*R*)-(salcy)CoCl, (*R*,*R*)-(salcy)CoBr, (*R*,*R*)-(salcy)CoOAc, and (*R*,*R*)-(salcy)CoOBzF$_5$ (OBzF$_5$ = pentafluorobenzoate) are highly active catalysts for the living, alternating copolymerization of propylene oxide (PO) and CO$_2$, yielding poly(propylene carbonate) (PPC) with no detectable byproducts. The PPC generated using these catalyst systems is highly regioregular and has up to 99% carbonate linkages with a narrow molecular weight distribution (MWD). Inclusion of the cocatalysts [PPN]Cl or [PPN][OBzF$_5$] ([PPN] = bis(triphenylphosphine)iminium) with complex (*R*,*R*)-(salcy)CoCl, (*R*,*R*)-(salcy)CoBr, or (*R*,*R*)-(salcy)CoOBzF$_5$ results in remarkable activity enhancement of the copolymerization as well as improved stereoselectivity and regioselectivity with maximized reactivity at low CO$_2$ pressures. In the case of [PPN]Cl with (*R*,*R*)-(salcy)CoOBzF$_5$, an unprecedented catalytic activity of 620 turnovers per hour is achieved for the copolymerization of *rac*-PO and CO$_2$, yielding iso-enriched PPC with 94% head-to-tail connectivity. The stereochemistry of the monomer and catalyst used in the copolymerization has dramatic effects on catalytic activity and the PPC microstructure. Using catalyst (*R*,*R*)-(salcy)CoBr with (*S*)-PO/CO$_2$ generates highly regioregular PPC, whereas using (*R*)-PO/CO$_2$ with the same catalyst gives an almost completely regiorandom copolymer. The *rac*-PO/CO$_2$ copolymerization with catalyst *rac*-(salcy)CoBr yields syndio-enriched PPC, an unreported PPC microstructure. In addition, (*R*,*R*)-(salcy)CoOBzF$_5$/[PPN]Cl copolymerizes (*S*)-PO and CO$_2$ with a turnover frequency of 1100 h^{-1}, an activity surpassing that observed in any previously reported system.

Introduction

CO$_2$ is an ideal synthetic feedstock because it is abundant, inexpensive, and nontoxic. Considerable interest in CO$_2$ activation with transition metal complexes is directed toward its use in organic synthesis.[1] One growing area in CO$_2$ chemistry is the development of catalysts for the alternating copolymerization of CO$_2$ and epoxides to form polycarbonates,[2] a field pioneered by Inoue and co-workers in the late 1960s.[3]

The copolymerization of CO$_2$ and alicyclic epoxides with discrete metal complexes has been well documented.[4−10] Aliphatic epoxides, such as propylene oxide (PO), remain a greater challenge owing to the concomitant production of cyclic carbonate as shown in Scheme 1.[5,6,8,10−14] The generalized

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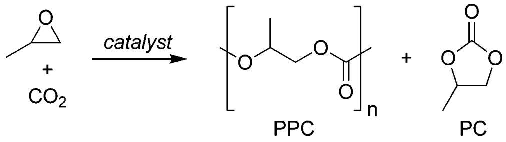
10.1021/ja051744l CCC: $30.25

Scheme 1. Reaction of Propylene Oxide and CO_2 to Yield Poly(propylene carbonate) and Propylene Carbonate



sequence for the PO/CO_2 copolymerization involves epoxide ring opening by a metal carbonate to give a metal alkoxide, followed by CO_2 insertion (Scheme 2). In addition, propylene carbonate (PC) can be formed through a back-biting reaction from the propagating alkoxide.[11]

Recent advances using β-diiminate zinc or salen-type (salen = *N*,*N′*-bis(salicylidene)-1,2-diaminoethane) chromium catalysts with Lewis base cocatalysts (Figure 1) have resulted in the highest reported activities for this reaction but produce significant quantities of the byproduct PC.[5,6,10−12] In an effort to improve selectivity for poly(propylene carbonate) (PPC) over PC, we searched for metal/ligand combinations known to effect stereo- and regioselective reactions with PO. Jacobsen and coworkers have reported chiral (salcy)Co^{III} carboxylates (salcy = *N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane) for the hydrolytic kinetic resolution of epoxides with remarkable efficiencies.[15] When we applied these catalysts to PO/CO_2 copolymerization, we observed unprecedented selectivity for highly regioregular PPC.[16] Specifically, (*R*,*R*)-(salcy)-CoOAc generated PPC with up to 99% carbonate linkages and 93% head-to-tail (HT) connectivity (Figure 2); however, it did not yield high number average molecular weights (M_ns), narrow molecular weight distributions (MWDs), or fast reaction rates characteristic of the zinc- and chromium-based alternatives.[5,6,10−12]

The coupling of porphyrin or salen-type metal catalysts with organic salt cocatalysts has resulted in improved catalytic activities in a variety of polymerization systems.[5,7,8,17−20] The addition of ammonium salt cocatalysts (n-Bu_4NY; Y = Cl, Br, I) to (*R*,*R*)-(salcy)CoX (X = OAc, O_2CCCl_3, O_2CCF_3, Cl, OTs; OTs = tosylate) complexes in the presence of PO and CO_2 shows reaction rates that are sensitive to the anionic components (X and Y) for the generation of PC.[21] Although it was originally thought that ammonium salt cocatalysts limited the (*R*,*R*)-(salcy)CoX catalyzed reaction of PO/CO_2 to the production of PC, PPC was recently achieved through the careful choice of the complex and cocatalyst.[20] Specifically, (*R*,*R*)-(salcy)CoOAr (OAr = 4-nitrophenoxy, 2,4-dinitrophenoxy, or 2,4,6-trinitrophenoxy) derivatives with $[n\text{-}Bu_4N]Y$ (Y = Cl, OAc) cocatalysts were described by Lu and co-workers to afford PPC with enhanced rates and selectivity. Since our discovery of the active (*R*,*R*)-(salcy)CoOAc system, we have furthered catalyst optimization, which has led to the use of organic salt cocatalysts as well.[5,7,8,17,20]

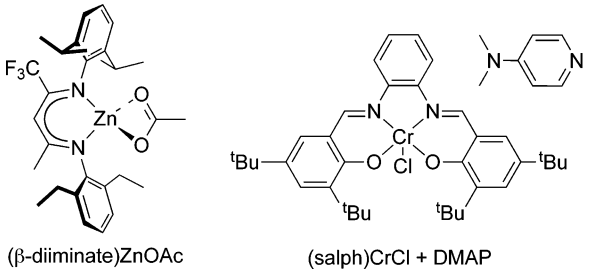


Figure 1. Catalysts for the copolymerization of propylene oxide and CO_2.

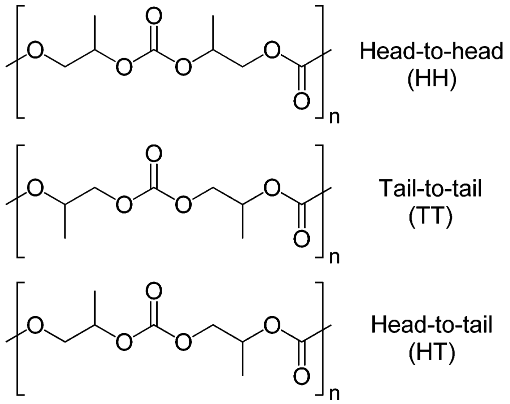


Figure 2. Regiochemistry of poly(propylene carbonate).

Herein, we present our continued studies concerning the PO/CO_2 copolymerization using (salcy)CoX complexes. We explore the influence of the catalyst initiator (X) on overall performance and investigate the effects of $[PPN]^+$-based ([PPN] = bis-(triphenylphosphine)iminium) ionic cocatalysts on catalyst activity, product selectivity, stereoselectivity, and regioselectivity. Additionally, we describe the diverse PPC stereo- and regiochemistries that result from variation of the catalyst and PO stereochemistry. These optimized systems demonstrate unprecedented reaction rates and selectivity while producing PPCs with high molecular weights and narrow MWDs.

Results and Discussion

Alternating Copolymerization of Propylene Oxide and Carbon Dioxide with (salcy)CoX Catalysts. We recently reported that (*R*,*R*)-(salcy)CoOAc catalyzes the alternating copolymerization of *rac*- or (*S*)-PO and CO_2 and exhibits unprecedented selectivity for PPC. Average turnover frequencies (TOFs), however, were limited to less than 85 h^{-1}.[16] In addition, the MWDs of PPC synthesized by (*R*,*R*)-(salcy)CoOAc were relatively broad (MWD = 1.2−2.6), and the measured M_n values of the polymers were lower than the corresponding theoretical values, results consistent with chain transfer to water throughout the copolymerization.[16] It has been shown that minor alterations in synthetic conditions and ligand structure can result in large differences in the catalytic performance of salen-type chromium complexes for epoxide/CO_2 copolymerization.[9] Herein, a detailed study of the copolymerization reaction conditions and nature of the initiating group and cocatalyst structure has provided for improved molecular weight control, increased polymerization activity, and mechanistic insight.

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Scheme 2. Copolymerization of Propylene Oxide and CO_2 Using Discrete Metal Alkoxides (R = OR′) and Carboxylates (R = Alkyl, Aryl)

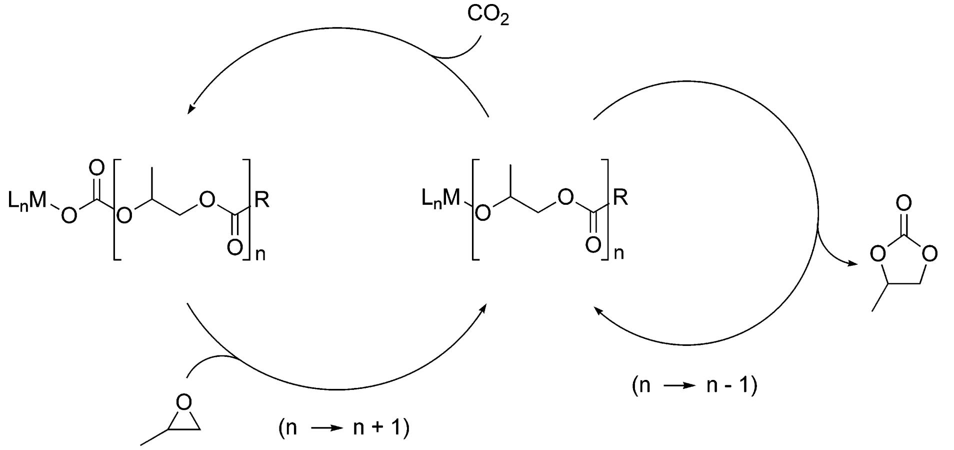
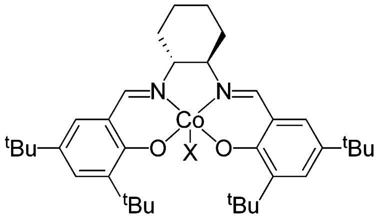


Table 1. Effect of Air-Free versus Ambient Reaction Conditions: (*R*,*R*)-(salcy)CoX Catalyzed Copolymerization of *rac*-PO/CO_2 (X = I, OAc)[a]

entry	complex	reaction conditions	time (h)	yield[b] (%)	TOF[c] (h^{-1})	theoretical M_n[d] (kg/mol)	M_n[e] (kg/mol)	M_w/M_n[e]	head-to-tail linkages[f] (%)
1	(*R*,*R*)-(salcy)CoI	air-free	5	43	43	21.9	19.6	1.15	79
2	(*R*,*R*)-(salcy)CoI	ambient	5	37	37	18.9	9.5	1.33	81
3	(*R*,*R*)-(salcy)CoOAc	air-free	2	30	75	15.3	15.5	1.16	83
4	(*R*,*R*)-(salcy)CoOAc	ambient	2	25	62	12.7	10.4	1.31	83

[a] Polymerizations run in neat *rac*-propylene oxide (PO) with [PO]/[Co] = 500:1 at 22 °C with 800 psi of CO_2. Selectivity for poly(propylene carbonate) (PPC) over propylene carbonate was >99% in all cases. All product PPC contains ≥96% carbonate linkages as determined by ^1H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency (TOF) = mol PO · mol Co^{-1} · h^{-1}. [d] Theoretical number average molecular weight (M_n) = TOF · h · 102 g/mol. [e] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [f] Determined by ^{13}C NMR spectroscopy.

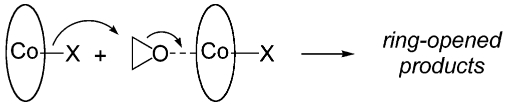


(*R*, *R*)-(Salcy)CoX
X = OAc, $OBzF_5$, Cl, Br, I

Figure 3. (Salcy)CoX catalysts for the copolymerization of propylene oxide and CO_2.

We initially carried out a comprehensive study of ligand modification with salen-type cobalt complexes in an effort to investigate the effects of altering the steric and electronic environment around the active cobalt center. To our surprise, the ligand that provided the most active catalyst while maintaining high regiocontrol was the original (salcy) ligand. (Salcy)CoX complexes were therefore used for further studies (Figure 3). We speculated that the (salcy)CoX systems would produce PPC with narrow MWDs by eliminating chain transfer agents such as water. As such, we thoroughly dried all (salcy)CoX complexes before use and performed the *rac*-PO/CO_2 copolymerization under air-free conditions. Table 1 compares the *rac*-PO/CO_2 copolymerizations carried out under air-free (entries 1 and 3) and ambient (entries 2 and 4) conditions using (*R*,*R*)-(salcy)CoI and (*R*,*R*)-(salcy)CoOAc catalysts. The PPC generated under air-free conditions exhibits a measured M_n that agrees more closely with the theoretical value and has a MWD less than 1.2. In all cases, PPC with ≥96% carbonate linkages and ≥79% HT connectivity was achieved with no detectable PC byproduct. Although the removal of trace water provides for a narrow MWD, it is not a necessary condition for the generation of PPC.

Scheme 3. Bimetallic (salcy)CoX (X = Nucleophile) Ring Opening of Epoxides Proposed by Jacobsen and Co-workers



Jacobsen and co-workers have conducted extensive studies that support a bimetallic mechanism for the chiral (salcy)CoX catalyzed kinetic resolution of terminal epoxides (Scheme 3).[22] With these systems, they observed a large reaction rate dependence on the composition of the axial ligand of the catalyst (X). These results led us to suspect that the nature of the axial ligand would likewise influence the rate of our PO/CO_2 copolymerizations. The polymerization data of complexes (*R*,*R*)-(salcy)CoX with X = OAc, pentafluorobenzoate ($OBzF_5$), Cl, Br, and I are collected in Table 2. Although the behavior of (*R*,*R*)-(salcy)CoOAc and (*R*,*R*)-(salcy)$CoOBzF_5$ proved largely similar (entries 1 and 2), use of the various halides ((*R*,*R*)-(salcy)CoCl, (*R*,*R*)-(salcy)CoBr, or (*R*,*R*)-(salcy)CoI) resulted in substantial changes in catalytic activity (entries 3−5). The order of increasing activity for copolymerization with (*R*,*R*)-(salcy)CoX complexes is $X = I < Cl < OAc \approx OBzF_5 < Br$, with the most active catalyst, (*R*,*R*)-(salcy)CoBr, producing PPC with a TOF = 90 h^{-1} (entry 4). Although catalyst activity varies with the applied axial ligand/initiator, we speculate that the propagation rates in all cases are inherently similar. Furthermore, we attribute the range of catalyst TOFs to an initiation period that occurs before polymer propagation. Similar to the bimetallic

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Table 2. Effect of Initiating Group: (*R*,*R*)-(salcy)CoX Catalyzed Copolymerization of *rac*-PO/CO_2 (X = OAc, $OBzF_5$, Cl, Br, I)[a]

entry	complex	yield[b] (%)	TOF[c] (h^{-1})	M_n[d] (kg/mol)	M_w/M_n[d]	head-to-tail linkages[e] (%)
1	(*R*,*R*)-(salcy)CoOAc	30	75	15.5	1.16	83
2	(*R*,*R*)-(salcy)$CoOBzF_5$	32	80	14.1	1.22	82
3	(*R*,*R*)-(salcy)CoCl	26	65	13.4	1.19	82
4	(*R*,*R*)-(salcy)CoBr	36	90	21.0	1.14	82
5	(*R*,*R*)-(salcy)CoI	13	33	10.4	1.17	85
6	(*R*,*R*)-(salcy)CoI + (*R*,*R*)-(salcy)CoBr (50:1)	28	70	16.2	1.24	81

[a] Polymerizations run in neat *rac*-propylene oxide (PO) with [PO]/[Co] = 500:1 at 22 °C with 800 psi of CO_2 for 2 h. Selectivity for poly(propylene carbonate) (PPC) over propylene carbonate was >99% in all cases. All product PPC contains ≥92% carbonate linkages as determined by ^1H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency (TOF) = mol PO · mol Co^{-1} · h^{-1}. [d] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [e] Determined by ^{13}C NMR spectroscopy. [$OBzF_5$] = pentafluorobenzoate.

mechanism proposed by Jacobsen and co-workers, we suspect that the rate in which the initiator is delivered from one cobalt center to ring open a PO bound to a second cobalt center depends on the Lewis acidity of the catalyst and the nucleophilicity of the axial ligand. Despite these initiation rate differences, all product PPCs are atactic with ≥92% carbonate linkages, ≥82% HT connectivity, and narrow MWDs. In addition, no detectable PC is observed in all systems.

Because the copolymerization rate exhibits a pronounced dependence on the nature of the axial ligand, we anticipated that through combining the slowest catalyst, (*R*,*R*)-(salcy)CoI, with the more active (*R*,*R*)-(salcy)CoBr, its copolymerization activity would improve. This prediction was indeed correct: as little as 2% of (*R*,*R*)-(salcy)CoBr with catalyst (*R*,*R*)-(salcy)CoI achieved a TOF of 70 h^{-1} while maintaining an overall [PO]:[Co] loading of 500:1 (Table 2, entry 6). This copolymerization rate is more than double that of the unassisted (*R*,*R*)-(salcy)CoI catalyzed reaction, even though [Br^-]:[I^-] is 1:50. PPC produced with the mixed catalyst system maintains 92% carbonate linkages and 81% HT connectivity although there is slight MWD broadening.

Alternating Copolymerization of Propylene Oxide and Carbon Dioxide with (salcy)CoX Catalysts and Ionic Cocatalysts. Previous reports have described improved catalytic activities upon the coupling of organic salt cocatalysts with porphyrin or salen-type catalysts for epoxide/CO_2 copolymerization.[5,7,8,17] Recently, Lu and co-workers described outstanding rates for the copolymerization of PO and CO_2 through the addition of quaternary ammonium salt cocatalysts to (salcy)CoX catalysts at low CO_2 pressures.[20] With the goal of increasing the catalytic activities of our systems, we independently explored the use of [PPN]Cl as a cocatalyst. [PPN]Cl is a commercially available, readily dried ionic compound with a bulky cation and a nucleophilic anion. We initially screened our catalyst library with [PPN]Cl for the *rac*-PO/CO_2 copolymerization at lower CO_2 pressures (200 psi) to look for an increase in reaction rates. We observed a remarkable improvement in catalyst activities, as well as increased stereo- and regioselectivities when [PPN]Cl was combined with any of the (*R*,*R*)-(salcy)CoX complexes (Table 3).

By itself, [PPN]Cl demonstrated no activity for the copolymerization of *rac*-PO and CO_2, whereas, in combination with complex (*R*,*R*)-(salcy)$CoOBzF_5$, PPC was generated with an activity of 520 turnovers per hour (Table 3, entry 2). The product PPC is nearly completely alternating, with >90% HT connectivity and is iso-enriched with a high M_n and a narrow MWD. Complexes (*R*,*R*)-(salcy)CoCl and (*R*,*R*)-(salcy)CoBr with [PPN]Cl also exhibit outstanding catalytic activity; however, selectivity for polymer is reduced with the latter (entries 3 and 4). The copolymerization catalyzed by (*R*,*R*)-(salcy)CoOAc with [PPN]Cl is significantly slower than that catalyzed by all other catalyst/[PPN]Cl combinations, and the selectivity for generating PPC over PC is also somewhat compromised (entry 1).

To optimize the reactivity of this catalyst system further, the influence of catalyst and cocatalyst ratio, reaction time, and CO_2 pressure on the copolymerization was investigated. The optimal loading for the *rac*-PO/CO_2 copolymerization with (*R*,*R*)-(salcy)$CoOBzF_5$ is a [PO]:[[PPN]Cl]:[Co] ratio of 2000:1:1 (Table 4, entries 1 and 2). Under these conditions, PPC is generated in 31% yield after 1 h and in 52% yield after 2 h, corresponding to catalyst TOFs of 620 h^{-1} and 520 h^{-1}, respectively, with only trace PC byproduct. At extended reaction times, however, the overall selectivity for polymer is decreased notably (entry 3). We observed that, at approximately 50% conversion, the polymerization solidifies, and the PPC slowly depolymerizes in situ to form PC. In an effort to maximize polymer yield, it is crucial to quench the copolymerization upon reaching approximately 50% conversion. To achieve PPC at higher % conversions, the addition of solvent is required, which is a subject under current investigation. Increasing the loading of [PPN]Cl to 2 equiv while maintaining 1 equiv of (*R*,*R*)-(salcy)$CoOBzF_5$ has no noticeable effect on the copolymerization (entry 4), whereas decreasing the [PPN]Cl content to 0.5 equiv results in a substantial loss in activity (entry 5). Overall, decreasing the amount of [PPN]Cl in the copolymerization while maintaining the same amount of catalyst and the same percent conversion increases the M_n of the product PPC. In great contrast to the performance of complex (*R*,*R*)-(salcy)$CoOBzF_5$ alone, the ion-assisted copolymerization is optimized at lower pressures of CO_2 (200 psi), suggesting the possibility of an alternate

Table 3. Effect of Initiating Group: (*R*,*R*)-(salcy)CoX Catalyzed Copolymerization of *rac*-PO/CO_2 with Cocatalyst [PPN]Cl (X = OAc, $OBzF_5$, Cl, Br)[a]

entry	complex	yield[b] (%)	TOF[c] (h^{-1})	selectivity[d] (% PPC)	M_n[e] (kg/mol)	M_w/M_n[e]	head-to-tail linkages[f] (%)
1	(*R*,*R*)-(salcy)CoOAc	11	110	86	47.9	1.15	93
2	(*R*,*R*)-(salcy)$CoOBzF_5$	52	520	>99	43.0	1.10	93
3	(*R*,*R*)-(salcy)CoCl	43	430	>99	35.4	1.09	95
4	(*R*,*R*)-(salcy)CoBr	46	460	89	33.2	1.09	95

[a] Polymerizations run in neat *rac*-propylene oxide (PO) with [PO]:[[PPN]Cl]:[Co] = 2000:1:1 at 22 °C with 200 psi of CO_2 for 2 h. All product poly(propylene carbonate) (PPC) contains ≥98% carbonate linkages as determined by ^1H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency = mol PO · mol Co^{-1} · h^{-1}. [d] Selectivity for PPC over propylene carbonate. [e] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [f] Determined by ^{13}C NMR spectroscopy. [PPN] = bis(triphenylphosphine)iminium. [$OBzF_5$] = pentafluorobenzoate.

Table 4. Effect of Cocatalyst [PPN]Cl Concentration and Reaction Time: (*R*,*R*)-(salcy)CoOBzF$_5$ Catalyzed Copolymerization of *rac*-PO/CO$_2$[a]

entry	[PO]:[[PPN]Cl]:[Co]	time ‘(h)	yield[b] (%)	TOF[c] (h^{-1})	selectivity[d] (% PPC)	M_n[e] (kg/mol)	M_w/M_n[e]	head-to-tail linkages[f] (%)
1	2000:1:1	1	31	620	99	26.8	1.13	94
2	2000:1:1	2	52	520	>99	43.0	1.10	93
3	2000:1:1	6	59	200	56	41.4	1.36	93
4	2000:2:1	2	53	530	97	33.9	1.08	93
5	2000:0.5:1	2	36	360	>99	46.3	1.07	94

[a] Polymerizations run in neat *rac*-propylene oxide (PO) at 22 °C with 200 psi of CO$_2$. All product poly(propylene carbonate) (PPC) contains ≥98% carbonate linkages as determined by ^{1}H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency = mol PO · mol Co^{-1} · h^{-1}. [d] Selectivity for PPC over propylene carbonate. [e] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [f] Determined by ^{13}C NMR spectroscopy. [PPN] = bis(triphenylphosphine)iminium. [OBzF$_5$] = pentafluorobenzoate.

Table 5. Effect of Cocatalyst and Initiator: (*R*,*R*)-(salcy)CoX Catalyzed Copolymerization of *rac*-PO/CO$_2$ (X = OBzF$_5$, Cl)[a]

entry	complex	cocatalyst	yield[b] (%)	TOF[c] (h^{-1})	selectivity[d] (% PPC)	M_n[e] (kg/mol)	M_w/M_n[e]	head-to-tail linkages[f] (%)
1	(*R*,*R*)-(salcy)CoOBzF$_5$	[PPN]Cl	52	520	>99	43.0	1.10	93
2	(*R*,*R*)-(salcy)CoOBzF$_5$	[*n*-Bu$_4$N]Cl	18	180	>99	7.6	1.13	94
3	(*R*,*R*)-(salcy)CoOBzF$_5$	[PPN][OBzF$_5$]	48	480	>99	51.9	1.14	94
4	(*R*,*R*)-(salcy)CoOBzF$_5$	[PPN][BPh$_4$]	0	0	NA	NA	NA	NA
5	(*R*,*R*)-(salcy)CoCl	[PPN][OBzF$_5$]	46	460	99	49.0	1.07	95

[a] Polymerizations run in neat *rac*-propylene oxide (PO) with [PO]:[cocatalyst]:[Co] = 2000:1:1 at 22 °C with 200 psi of CO$_2$ for 2 h. All product poly(propylene carbonate) (PPC) contains ≥98% carbonate linkages as determined by ^{1}H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency = mol PO · mol Co^{-1} · h^{-1}. [d] Selectivity for PPC over propylene carbonate. [e] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [f] Determined by ^{13}C NMR spectroscopy. [PPN] = bis(triphenylphosphine)iminium. [OBzF$_5$] = pentafluorobenzoate.

mechanism. We suspect that the ionic cocatalyst helps to stabilize the active species against decomposition to (*R*,*R*)-(salcy)Co^{II}, a reaction that is observed with these catalysts alone at low CO$_2$ pressures.[23] Indeed, with the incorporation of [PPN]-Cl, PPC can be generated at pressures as low as 50 psi with only slightly compromising activity and selectivity for polymer.

By altering the composition of the ionic cocatalyst, we obtained information about how the cation and anion influence the *rac*-PO/CO$_2$ copolymerization. Replacement of [PPN]Cl with [*n*-Bu$_4$N]Cl results in a notable decrease in activity (Table 5, entries 1 and 2). PPC generated by (*R*,*R*)-(salcy)CoOBzF$_5$ with [*n*-Bu$_4$N]Cl has a low M_n attributable to chain transfer to water introduced by the ammonium salt. Substitution of [PPN]-[OBzF$_5$] for [PPN]Cl with complex (*R*,*R*)-(salcy)CoOBzF$_5$ has little effect on the reaction rate (entry 3), but the reaction with the salt [PPN][BPh$_4$] shows a complete loss in activity (entry 4). In general, a bulky noncoordinating cation and a nucleophilic anion capable of initiation compose the ideal cocatalyst for the (*R*,*R*)-(salcy)CoOBzF$_5$ catalyzed copolymerization; [PPN]Cl and [PPN][OBzF$_5$] are most beneficial.

The M_n values of the polymers obtained from the ion-assisted copolymerizations are reproducible and approach 50 kg/mol, yet they are equal to approximately half of the theoretical values based on conversion. We suspect that initiation is not limited to the original initiating group of the cobalt catalyst but also involves the anion from the [PPN]$^+$ cocatalyst. To demonstrate this possibility, PPC was prepared with two different catalyst/cocatalyst combinations: (*R*,*R*)-(salcy)CoOBzF$_5$/[PPN]Cl and (*R*,*R*)-(salcy)CoCl/[PPN][OBzF$_5$]. The isolated polymer from each system exhibited an M_n of approximately 10 kg/mol with a narrow MWD and showed UV activity by the gel permeation chromatography (GPC) UV detector. In addition, the ^{19}F NMR spectrum of each polymer revealed that OBzF$_5$ end groups were present in both samples. Each spectrum exhibited ^{19}F resonances at δ −138 (m), −149 (m), −161 (m) ppm, consistent with a OBzF$_5$ moiety on the PPC. These data suggest that initiation can occur from the catalyst precursor as well as the salt cocatalyst. Furthermore, as there are two feasible initiators per catalyst and product PPCs exhibit M_n values approximately half those of the theoretical values with narrow MWDs, we hypothesize that each cobalt center propagates two polymer chains.

The addition of a Lewis base cocatalyst to epoxide/CO$_2$ copolymerizations with porphyrin or salen-type metal catalysts has provided for enhanced catalytic activities in a variety of systems.[5,6,9,10,12,17,24] In several of these cases a proposed mechanism illustrates that the Lewis base coordinates to the metal center in the axial site, trans to the propagating species, resulting in an improved electronic environment for propagation. In agreement with these schemes, we consider that the axial ligand trans to the propagating species has a large influence on the propagation rate. As we suspect that the anion of the ionic cocatalyst in our systems is capable of initiation, we hypothesize that two polymer chains can simultaneously propagate from either side of the Co-salcy plane (Scheme 4), a mechanism similar to that proposed by Inoue and co-workers using aluminum porphyrins and ammonium and phosphonium salts.[17]

Influence of Catalyst and Propylene Oxide Stereochemistry on Catalytic Activity and Polymer Microstructure. We previously reported that catalyst (*R*,*R*)-(salcy)CoOAc preferentially enchains (*S*)-PO over (*R*)-PO (k_{rel} = 2.8) in *rac*-PO/CO$_2$ copolymerization.[16] Also, substitution of (*S*)-PO for *rac*-PO increases the HT connectivity of the product PPC from 80% to 93%. These initial experiments indicate that the chiralities of the monomer and the catalyst strongly influence the polymerization activities and the product PPC regiochemistry. Furthermore, the relationship among the catalyst and PO stereochem-

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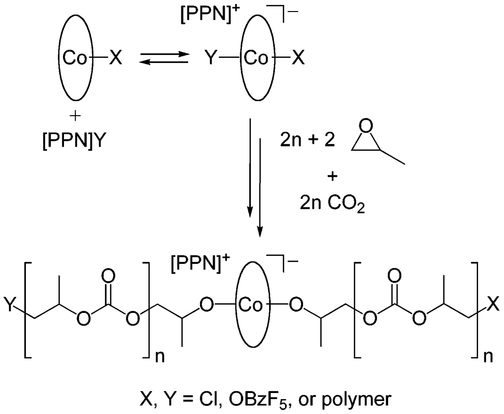
[23] When the PO/CO$_2$ copolymerization is carried out at low CO$_2$ pressures (<100 psi) in a Fischer−Porter bottle, the reduction of (*R*,*R*)-(salcy)Co^{III}X to (*R*,*R*)-(salcy)Co^{II} can be observed as a red solid (Co^{II}) precipitates from the reaction. This reaction is also thought to occur at higher CO$_2$ pressures; however the CO$_2$ must be vented from the Parr reactor before we are able to look at the reaction mixture, preventing direct observation.

Table 6. (*R*,*R*)- and *rac*-(salcy)CoBr Catalyzed Copolymerization of PO/CO_2 Using *rac*-, (*S*)-, and (*R*)-PO[a]

entry	complex	epoxide	yield[b] (%)	TOF[c] (h^{-1})	M_n[d] (kg/mol)	M_w/M_n[d]	head-to-tail linkages[e] (%)
1	(*R*,*R*)-(salcy)CoBr	*rac*-PO	36	90	21.0	1.14	82
2	(*R*,*R*)-(salcy)CoBr	(*S*)-PO	49	120	20.1	1.21	93
3	(*R*,*R*)-(salcy)CoBr	(*R*)-PO	20	50	13.3	1.16	43
4	*rac*-(salcy)CoBr	(*R*)-PO	42	110	26.9	1.16	83
5	*rac*-(salcy)CoBr	*rac*-PO	41	100	21.8	1.22	84

[a] Polymerizations run in neat propylene oxide (PO) with [PO]/[Co] = 500:1 at 22 °C with 800 psi of CO_2 for 2 h. Selectivity for poly(propylene carbonate) (PPC) over propylene carbonate was >99% in all cases. All product PPC contains ≥92% carbonate linkages as determined by ^1H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency (TOF) = mol PO · mol Co^{-1} · h^{-1}. [d] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [e] Determined by ^{13}C NMR spectroscopy.

Scheme 4. Proposed Scheme for the Copolymerization of Propylene Oxide and CO_2 with Catalyst (salcy)CoX and Cocatalyst [PPN]Y; [PPN] = Bis(triphenylphosphine)iminium, [$OBzF_5$] = Pentafluorobenzoate



istry and the resultant PPC microstructure provides mechanistic insight.[25] As such, we were eager to pursue this topic with the (salcy)CoBr and (salcy)$CoOBzF_5$/[PPN]Cl catalyst systems.

Table 6 lists the copolymerization data for (*R*,*R*)-(salcy)CoBr and *rac*-(salcy)CoBr with *rac*-, (*S*)-, and (*R*)-PO. As stated above, the copolymerization of *rac*-PO and CO_2 with catalyst (*R*,*R*)-(salcy)CoBr produces atactic PPC with 82% HT connectivity (entry 1, Figure 4a, and Scheme 5a). Under the same reaction conditions, but replacing *rac*-PO with (*S*)-PO, the catalytic activity increases from 90 to 120 turnovers per hour, and the resultant PPC is isotactic with 93% HT connectivity (entry 2, Figure 4b, and Scheme 5b). This result is consistent with our earlier work[16] and indicates that the (*R*,*R*) catalyst makes fewer regioerrors when only (*S*)-PO is present. Degradation of this polymer to PC while conserving all stereocenters[14] yielded an (*S*)-PC:(*R*)-PC ratio of 97:3 as determined by gas chromatography (GC). The high (*S*)-content of the PPC suggests that transcarbonation and PC reinsertion mechanisms do not readily occur and that the PO ring opening process predominately takes place at the methylene or methine carbon with stereochemical retention. Chisholm and co-workers have previously shown the possibility of PO ring opening at the methine carbon with stereochemical retention in related chromium and aluminum catalyst systems.[24] Although a consistent methine (*S*)-PO ring opening process with stereochemical retention would result in PPC with a high (*S*) content, we believe that the preferred reaction pathway in our systems is the sterically favored attack at the methylene carbon.

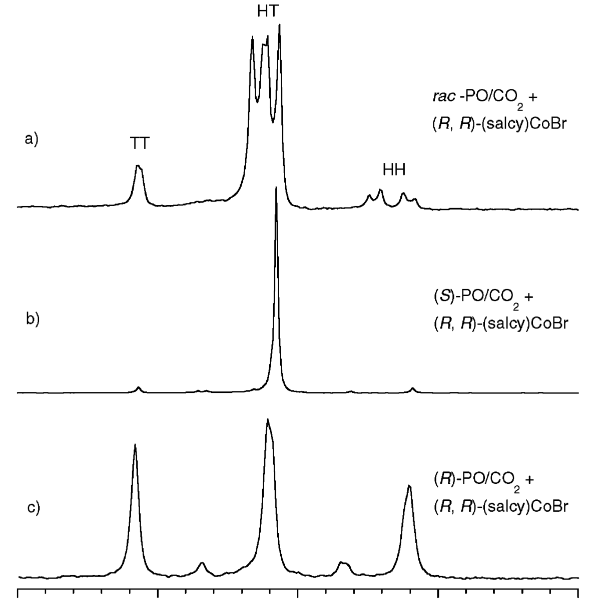


Figure 4. Carbonyl region of the ^{13}C NMR spectra (125 MHz, $CDCl_3$) of poly(propylene carbonate)s generated from the copolymerization of a) *rac*-propylene oxide (PO)/CO_2, b) (*S*)-PO/CO_2, and c) (*R*)-PO/CO_2 with catalyst (*R*,*R*)-(salcy)CoBr. TT = tail-to-tail; HT = head-to-tail; HH = head-to-head.

When (*R*)-PO is used in place of *rac*-PO, catalytic activity decreases to 50 turnovers per hour and the resultant PPC is almost perfectly regiorandom with only 43% HT connectivity (Table 6, entry 3, Figure 4c, and Scheme 5c). In this case, degradation of the polymer to PC yields a (*S*)-PC:(*R*)-PC ratio of 34:66. Assuming PO methine attack inverts stereochemistry, while methylene attack retains stereochemistry, a HH or TT linkage in the polymer requires one (*S*)- and one (*R*)-stereocenter. Furthermore, the excess of (*R*)-PC illustrates that the HT connectivity of the parent PPC is composed of predominately (*R*)-stereocenters. This indicates that generation of an HH linkage through misinsertion is most often immediately corrected to generate a TT linkage, followed by the incorporation of a couple of (*R*)-HT linkages until the next regioerror occurs.

We proceeded to replace the (*R*,*R*)-(salcy)CoBr complex with *rac*-(salcy)CoBr in order to obtain further mechanistic insight concerning propagation with these systems. The copolymerization of (*R*)-PO and CO_2 with *rac*-(salcy)CoBr yielded isotactic PPC with 83% HT connectivity with a catalytic activity of 110 turnovers per hour (Table 6, entry 4, and Scheme 5d). In this case, we expected two polymers with widely differing M_n values due to the predicted distinction in activity between the (*S*,*S*)- and (*R*,*R*)-(salcy)CoBr catalysts with (*R*)-PO/CO_2. Interestingly, the product PPC showed a monomodal GPC trace with a MWD

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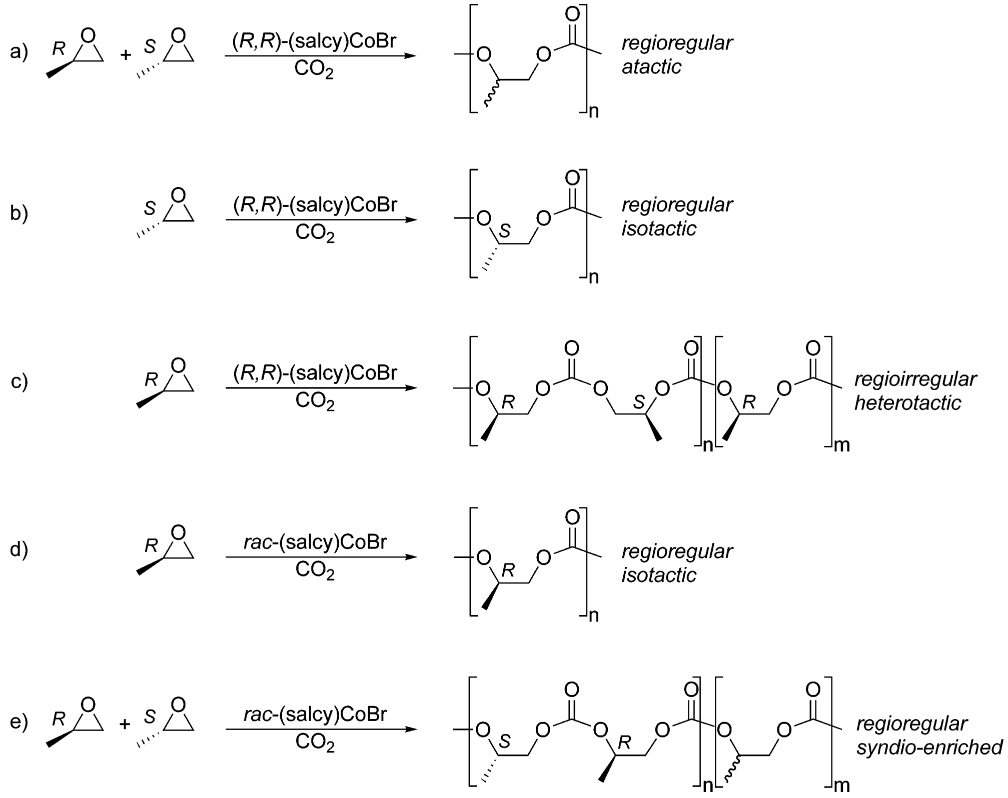
(24) Chisholm, M. H.; Zhou, Z. P. *J. Am. Chem. Soc.* **2004**, *126*, 11030−11039.
(25) Byrnes, M. J.; Chisholm, M. H.; Hadad, C. M.; Zhou, Z. P. *Macromolecules* **2004**, *37*, 4139−4145.

Scheme 5. Effect of Propylene Oxide and (salcy)CoBr Stereochemistry on Poly(propylene carbonate) Microstructure



of 1.16, suggesting that each propagating species can dissociate from the metal center during the copolymerization and is influenced by catalysts of both possible chiralities. The degradation PC product from this polymer has a (*S*)-PC:(*R*)-PC ratio of 9:91, again illustrating that regioerrors are immediately corrected.

Finally, we investigated the *rac*-PO/CO_2 copolymerization with catalyst *rac*-(salcy)CoBr. To our surprise, the product PPC, with 84% HT connectivity, has a ^{13}C NMR spectrum unlike that of all other PPC samples (Table 6, entry 5, Figure 5, and Scheme 5e).[26] In this case, the carbonyl resonances corresponding to the four HT triads ([mm], [mr], [rm], and [rr]) did not show an equal distribution. We initially assigned the most upfield HT shift in this spectrum as the [mm] triad (Figure 5) based on the observation that the ^{13}C NMR HT resonance of isotactic PPC aligns with the most upfield HT resonance of atactic PPC (Figure 4a,b). Furthermore, the [mr] and [rm] HT linkages should integrate equally yet show different resonances due to the directionality in the PPC. We therefore tentatively assigned the central HT resonances to the [mr]/[rm] triads and the remaining [rr] triad to the most downfield HT resonance, while considering that most tactic polymer systems exhibit [mm] and [rr] resonances that encompass the [mr]/[rm] ^{13}C NMR resonances.[27,28] Based on this scheme, we assigned the most downfield and upfield resonances in both the TT and HH portions of the spectrum to [r] and [m] diads, respectively, a simplification of the complex triad sequences from the many possible combinations of neighboring stereo- and regiosequences. It is also notable that the TT [m] and [r], HT [m] and [r], and HH [m] and [r] linkages of PPC as well as the HH [mmm] and [rrr] linkages of oligoether carbonates have been previously assigned by Chisholm and co-workers[24,25] and are in agreement with our PPC conformational assignments discussed above.

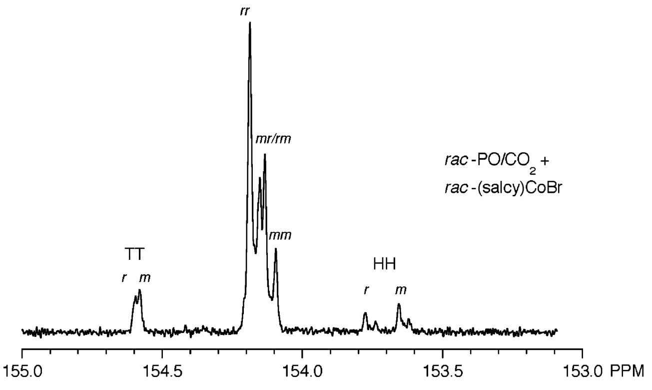


Figure 5. Carbonyl region of the ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of poly(propylene carbonate) generated from the copolymerization of *rac*-propylene oxide/CO_2 with catalyst *rac*-(salcy)CoBr. TT = tail-to-tail; HT = head-to-tail; HH = head-to-head.

Based on our ^{13}C NMR assignments, the HT portion of the PPC generated from *rac*-PO/CO_2 with catalyst *rac*-(salcy)CoBr is syndio-enriched, an unreported microstructure for this polymer system. As the regioregularity in the PPC implicates that the PO ring-opening event occurs consistently at the less substituted carbon, we suspect that the PPC syndiotacticity is achieved through a chain-end control mechanism, with alternate enchainment of (*S*)- and (*R*)-PO.[29] Specifically, assuming that the enchainment of (*S*)- over (*R*)-PO is favored for catalyst (*R*,*R*)-

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(26) A 30° shifted squared sinusoidal window function was applied prior to Fourier transformation in order to enhance resolution.

(27) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.

(28) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 1337−1343.

(29) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316−1326.

Table 7. (R,R)- and *rac*-(salcy)CoOBzF$_5$ Catalyzed Copolymerization of PO/CO$_2$ with Cocatalyst [PPN]Cl Using *rac*-, (S)-, and (R)-PO[a]

entry	complex	epoxide	time (h)	yield[b] (%)	TOF[c] (h^{-1})	selectivity[d] (%PPC)	M_n[e] (kg/mol)	M_w/M_n[e]	head-to-tail linkages (%)
1	(R,R)-(salcy)CoOBzF$_5$	*rac*-PO	1	31	620	99	26.8	1.13	94
2	(R,R)-(salcy)CoOBzF$_5$	(S)-PO	0.5	27	1100	>99	22.2	1.15	96
3	(R,R)-(salcy)CoOBzF$_5$	(R)-PO	2	21	210	98	19.1	1.12	87
4	*rac*-(salcy)CoOBzF$_5$	(R)-PO	1	37	740	>99	34.5	1.07	95
5	*rac*-(salcy)CoOBzF$_5$	*rac*-PO	1	33	660	>99	32.7	1.10	95

[a] Polymerizations run in neat propylene oxide (PO) with [PO]:[[PPN]Cl]:[Co] = 2000:1:1 at 22 °C with 200 psi of CO$_2$. All product poly(propylene carbonate) (PPC) contains ≥98% carbonate linkages as determined by ^{1}H NMR spectroscopy. [b] Based on isolated polymer yield. [c] Turnover frequency (TOF) = mol PO · mol Co^{-1} · h^{-1}. Selectivity for PPC over propylene carbonate. [e] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [f] Determined by ^{13}C NMR spectroscopy. [PPN] = bis(triphenylphosphine)iminium. [OBzF$_5$] = pentafluorobenzoate.

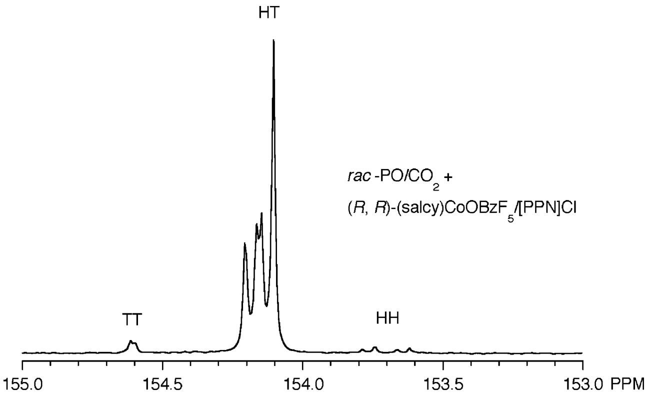

Figure 6. Carbonyl region of the ^{13}C NMR spectrum (125 MHz, CDCl$_3$) of poly(propylene carbonate) generated from the copolymerization of *rac*-propylene oxide/CO$_2$ with catalyst (R,R)-(salcy)CoOBzF$_5$/[PPN]Cl. TT = tail-to-tail; HT = head-to-tail; HH = head-to-head.

(salcy)CoBr and that the carboxylate generated from subsequent CO$_2$ insertion can migrate between cobalt centers, an (R,R)-(salcy)CoBr catalyst will ring open an (S)-PO and insert CO$_2$ and then the propagating carboxylate will migrate to an (S,S)-(salcy)CoBr catalyst before the next PO insertion occurs.

The mechanistic insight obtained from the stereochemical experiments with (salcy)CoBr led us to pursue similar studies with the (salcy)CoOBzF$_5$/[PPN]Cl catalyst systems. Table 7 shows the copolymerization data for (R,R)-(salcy)CoOBzF$_5$/[PPN]Cl and *rac*-(salcy)CoOBzF$_5$/[PPN]Cl with *rac*-, (S)-, and (R)-PO/CO$_2$. Remarkably, the addition of [PPN]Cl to the (R,R)-(salcy)CoOBzF$_5$ catalyzed *rac*-PO/CO$_2$ copolymerization not only increases the catalytic activity but also improves the stereo- and regioselectivity of the catalyst. Specifically, (R,R)-(salcy)-CoOBzF$_5$/[PPN]Cl demonstrates an activity of 620 turnovers per hour for the copolymerization of *rac*-PO and CO$_2$, affording iso-enriched PPC with 94% HT connectivity (entry 1, and Figure 6). The substitution of (S)-PO for *rac*-PO in this copolymerization results in a near doubling of the reaction rate (TOF = 1100 h^{-1}), affording highly alternating, isotactic PPC with 96% HT connectivity (entry 2). Alternatively, the substitution of (R)-PO for *rac*-PO in the copolymerization results in substantial rate inhibition in which a TOF of only 210 h^{-1} is achieved (entry 3). The product PPC from this reaction is isotactic and has 87% HT connectivity, showing that the regioselectivity of this system is less dependent on the relative stereochemistry of PO and catalyst than was observed with (salcy)CoBr.

The copolymerization of (R)-PO/CO$_2$ with catalyst *rac*-(salcy)CoOBzF$_5$ and [PPN]Cl yields isotactic PPC with 95% HT connectivity (Table 7, entry 4). This polymer shows a monomodal GPC trace with an MWD of 1.07. Similar to that discussed above, this result supports a mechanism in which each propagating species can dissociate from the metal center during the copolymerization and is influenced by catalysts of both possible chiralities.

Using catalyst *rac*-(salcy)CoOBzF$_5$ with [PPN]Cl for the copolymerization of *rac*-PO and CO$_2$ yields atactic PPC with 95% HT connectivity (Table 7, entry 5). Unlike the corresponding results using *rac*-(salcy)CoBr alone (Table 6, entry 5, and Figure 5), the PPC microstructures generated by *rac*-(salcy)-CoOBzF$_5$/[PPN]Cl or (R,R)-(salcy)CoOBzF$_5$/[PPN]Cl catalyst systems are essentially the same for the *rac*-PO/CO$_2$ copolymerization. Our experiments with catalysts (salcy)CoX for the PO/CO$_2$ copolymerization have led us to the following mechanistic assertions. The influence of the initiator on the copolymerization rate and the effect of combining different (salcy)CoX catalysts, where a fast initiator can assist a slower one, support a bimetallic initiation similar to that proposed by Jacobsen and co-workers for the hydrolytic kinetic resolution of epoxides.[22] Additionally, the relationship of the PO and catalyst stereochemistry to the resultant PPC microstructure is consistent with a scheme in which the propagating species can dissociate from the metal center during the copolymerization.

Our working hypothesis for the PO/CO$_2$ copolymerization with (salcy)CoX and ionic cocatalysts stems from the observation that the (salcy)CoX initiator and the cocatalyst anion can be found as end groups on the resultant PPC. This suggests that initiation can occur with either of these species, which is further corroborated by the measured M_n data, which are approximately half those of the corresponding theoretical values based on conversion. As previously discussed, we propose a mechanism in which propagation can occur simultaneously on either side of the Co-salcy plane (Scheme 4). In addition, our results support that the propagating species can dissociate from the metal center during the copolymerization, a mechanism similar to that of the (salcy)CoBr catalyzed copolymerization in the absence of cocatalyst.

Conclusions

We have investigated a series of cobalt-based (salcy) catalysts for the copolymerization of PO and CO$_2$. Through adjustment of the reaction environment and catalyst optimization we were able to maximize catalytic activity and selectivity for the generation of highly alternating, regioregular PPC with controlled molecular weight and no detectable PC byproduct. Through supplementation of the cobalt catalysts with [PPN]Cl or [PPN][OBzF$_5$] cocatalysts, we effected dramatic changes in polymerization behavior, catalytic activity, and regioselectivity. The PO/CO$_2$ copolymerization with (salcy)CoX (X = Cl, OBzF$_5$) and [PPN]Cl or [PPN][OBzF$_5$] effected increased catalytic activities, enhanced stereo- and regioselectivities, with maximized reactivity at low CO_2 pressures. The copolymerization of *rac*-PO and CO_2 with (*R*,*R*)-(salcy)CoOBzF$_5$ and [PPN]Cl yielded a TOF of 620 h^{-1} for iso-enriched PPC with 94% HT connectivity. By varying catalyst and PO stereochemistry, we observed pronounced alterations in the resultant PPC microstructure, as well as changes in catalytic activity. The copolymerization of *rac*-PO/CO_2 with catalyst *rac*-(salcy)CoBr yielded syndio-enriched PPC, an unreported microstructure for this polymer. The copolymerization of (*S*)-PO and CO_2 with catalyst (*R*,*R*)-(salcy)CoOBzF$_5$ and cocatalyst [PPN]Cl displayed a TOF = 1100 h^{-1} for isotactic PPC. To our knowledge, these catalyst systems exhibit the highest activities for the copolymerization of PO and CO_2, as well as maintain excellent selectivity for polymer with regiocontrol and living behavior. Given the overall success with these systems for the synthesis of PPC, our current focus is the study of (salcy)CoX catalyzed copolymerizations in greater mechanistic detail.

Experimental Section

General Procedure. All air or water sensitive reactions were carried out under dry nitrogen using a Braun Labmaster drybox or standard Schlenk-line techniques. Methylene chloride and diethyl ether were dried and degassed by passing through a column of activated alumina and by sparging with dry nitrogen. (*S*,*S*)- and (*R*,*R*)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexanecobalt ((*S*,*S*)-(salcy)Co^{II}, (*R*,*R*)-(salcy)Co^{II}) were purchased from Aldrich and recrystallized from methylene chloride and methanol. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) was purchased from Strem and recrystallized from dry methylene chloride and diethyl ether under nitrogen before use. Bis(triphenylphosphine)iminium tetraphenylborate ([PPN][BPh$_4$]) was prepared following literature procedure.[30,31] PO was dried over calcium hydride and vacuum transferred before use. CO_2 (99.998% purity) was purchased from Airgas and passed over a column of activated 4 Å molecular sieves. All other reagents were purchased from commercial sources and used as received. Degradation of PPC to PC was performed according to literature procedure,[14] and the product PC was analyzed by GC. Gas chromatograms were obtained on a Hewlett-Packard 6890 series gas chromatograph using a beta-DEX 225 chiral capillary column (30.0 m × 250 μm × 0.25 μm nominal), a flame ionization detector, and He carrier gas. Varian Mercury (300 MHz), Varian Inova (500 MHz), and Varian Inova (600 MHz) spectrometers were used to record ^{13}C and ^{1}H NMR spectra, which were referenced versus residual nondeuterated solvent shifts. C_6F_6 (−162.90 ppm) was used as a reference for all ^{19}F NMR spectra. GPC analyses were carried out using a Waters instrument (M515 pump, U6K injector) equipped with a Waters UV486 and Waters 2410 differential refractive index detector and four 5 μm PL Gel columns (Polymer Laboratories; 100 Å, 500 Å, 1000 Å, and Mixed C porosities) in series. The GPC columns were eluted with THF at 40 °C at 1 mL/min and were calibrated using 23 monodisperse polystyrene standards. Elemental analyses were carried out by Robertson Microlit Laboratories in Madison, NJ.

Complex Synthesis. Oxidation of the commercially available (*R*,*R*)-(salcy)Co^{II} readily occurs in the presence of a variety of acids to yield (*R*,*R*)-(salcy)CoOAc,[15] (*R*,*R*)-(salcy)CoOTs (OTs = tosylate),[22] and (*R*,*R*)-(salcy)CoOBzF$_5$. Complex (*R*,*R*)-(salcy)CoOTs can be further modified through metathesis reactions with the desired NaX salt, affording (*R*,*R*)-(salcy)CoX (X = Cl, Br, I).[22] Alternatively, *rac*-(salcy)-CoX catalysts are prepared using the same procedures listed above but starting with a 50:50 mixture of (*R*,*R*)-(salcy)Co^{II} and (*S*,*S*)-(salcy)-Co^{II}.

(*R*,*R*)-(salcy)CoOAc. The preparation of (*R*,*R*)-(salcy)CoOAc has been described previously by Jacobsen and co-workers;[15] however, only 1 equiv of acetic acid was used.

(*R*,*R*)-(salcy)CoCl. This complex was prepared as previously described.[22] Additional characterization: ^{13}C NMR (DMSO-d_6, 125 MHz): δ 24.34, 29.51, 30.40, 31.56, 33.51, 35.78, 69.27, 118.58, 128.78, 129.28, 135.86, 141.84, 162.08, 164.68.

(*R*,*R*)-(salcy)CoBr and ***rac*-(salcy)CoBr.** The procedure for the synthesis of (*R*,*R*)-(salcy)CoCl published by Jacobsen and co-workers[22] was applied to the synthesis of complexes (*R*,*R*)-(salcy)CoBr and *rac*-(salcy)CoBr, with the substitution of NaBr for NaCl. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.30 (s, 18H), 1.58 (m, 2H), 1.74 (s, 18H), 1.92 (m, 2H), 2.00 (m, 2H), 3.06 (m, 2H), 3.59 (m, 2H), 7.44 (d, ^4J = 3.0 Hz, 2H), 7.47 (d, ^4J = 3.0 Hz, 2H), 7.83 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 24.32, 29.57, 30.43, 31.55, 33.58, 35.82, 69.32, 118.61, 128.78, 129.28, 135.87, 141.84, 162.11, 164.66. Anal. Calcd for $C_{36}H_{52}N_2O_2CoBr$: C, 63.25; H, 7.67; N, 4.10. Found: C, 63.05; H, 7.69; N, 4.06.

(*R*,*R*)-(salcy)CoI. The procedure for the synthesis of (*R*,*R*)-(salcy)-CoCl published by Jacobsen and co-workers[22] was applied to the synthesis of complex (*R*,*R*)-(salcy)CoI, with the substitution of NaI for NaCl. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.32 (s, 18H) 1.63 (m, 2H), 1.76 (s, 18H), 1.91 (m, 2H), 2.02 (m, 2H), 3.10 (m, 2H), 3.66 (m, 2H), 7.45 (d, ^4J = 2.5 Hz, 2H), 7.50 (d, ^4J = 2.5 Hz, 2H), 7.83 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 24.23, 29.54, 30.36, 31.49, 33.47, 35.71, 69.22, 118.59, 128.63, 129.16, 135.82, 141.74, 161.95, 164.49. Anal. Calcd for $C_{36}H_{52}N_2O_2CoI$: C, 59.18; H, 7.17; N, 3.83. Found: C, 59.14; H, 7.05; N, 3.75.

(*R*,*R*)-(salcy)CoOBzF$_5$ and *rac*-(salcy)CoOBzF$_5$. Recrystallized (*R*,*R*)-(salcy)Co^{II} or *rac*-(salcy)Co^{II} (1.2 g, 2.0 mmol) and pentafluorobenzoic acid (0.42 g, 2.0 mmol) were added to a 50 mL round-bottomed flask charged with a Teflon stir bar. Toluene (20 mL) was added to the reaction mixture, and it was stirred open to air at 22 °C for 12 h. The solvent was removed by rotary evaporation at 22 °C, and the solid was suspended in 200 mL of pentane and filtered. The dark green crude material was dried in vacuo and collected in quantitative yield. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.30 (s, 18H), 1.59 (m, 2H), 1.74 (s, 18H), 1.90 (m, 2H), 2.00 (m, 2H), 3.07 (m, 2H), 3.60 (m, 2H), 7.44 (d, ^4J = 2.5 Hz, 2H), 7.47 (d, ^4J = 3.0 Hz, 2H), 7.81 (s, 2H).^{13}C NMR (DMSO-d_6, 125 MHz): δ 24.39, 29.61, 30.13, 30.42, 31.55, 33.57, 35.83, 69.38, 118.59, 128.78, 129.29, 135.86, 141.83, 162.21, 164.66. Carbons on the phenyl group of pentafluorobenzoate were not assigned in the ^{13}C NMR spectrum owing to complex carbon fluorine splitting patterns.^{19}F NMR (470 MHz, DMSO-d_6): δ −163.32 (m), −162.50 (m), −144.48 (m). Anal. Calcd for $C_{43}H_{52}O_4N_2F_5Co{\cdot}H_2O$: C, 62.01; H, 6.54; N, 3.36. Found: C, 62.25; H, 6.38; N, 3.42.

[PPN][OBzF$_5$]. NaOH (0.19 g, 4.7 mmol) and pentafluorobenzoic acid (1.0 g, 4.7 mmol) were added to a 50 mL round-bottomed flask charged with a Teflon stir bar. Distilled H_2O (20 mL) was added to the reaction mixture, and it was stirred until all was dissolved. The solution was added to a 250 mL separatory funnel along with [PPN]Cl (0.40 g, 0.70 mmol) and methylene chloride (40 mL), and the mixture was shaken vigorously for 10 min. The organic layer was collected and dried by rotary evaporation to yield crude [PPN][OBzF$_5$] in quantitative yield. Precipitation from dry methylene chloride and diethyl ether under N_2 at −20 °C afforded a white powder (0.35 g, 67%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.39−7.46 (m, 24H), 7.60−7.63 (m, 6H).^{13}C NMR (CDCl$_3$, 125 MHz): δ 116.93, 126.91 (dd, $^1J_{P-C}$ = 108.0 Hz, $^3J_{P-C}$ = 1.5 Hz), 129.55 (m), 132.02 (m), 133.88, 137.07 (d of m, $^1J_{F-C}$ = 255.5 Hz), 139.92 (d of m, $^1J_{F-C}$ = 250.3 Hz), 143.24 (d of m, $^1J_{F-C}$ = 247.3 Hz), 161.21. ^{19}F NMR (470 MHz, CDCl$_3$): δ −164.64 (m), −159.92 (broad s), −142.52 (m). Anal. Calcd for $C_{43}H_{30}F_5NO_2P_2$: C, 68.89; H, 4.03; N, 1.87. Found: C, 69.07; H, 3.95; N, 1.83.

Representative Copolymerization Procedure. A 100 mL Parr autoclave was heated to 120 °C under vacuum for 4 h, then cooled

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under vacuum to 22 °C, and moved to a drybox. Complex (*R*,*R*)-(salcy)-$CoOBzF_5$ (11.7 mg, 0.0143 mmol), cocatalyst [PPN]Cl (8.2 mg, 0.014 mmol), and *rac*-PO (2.00 mL, 28.6 mmol) were placed in a glass sleeve with a Teflon stir bar inside the Parr autoclave. The autoclave was pressurized to 200 psi of CO_2 and was left to stir at 22 °C for 1 h. The reactor was vented at 22 °C. A small aliquot of the resultant polymerization mixture was removed from the reactor for ^1H NMR and GPC analysis. The remaining polymerization mixture was then dissolved in methylene chloride (5 mL), quenched with 5% HCl solution in methanol (0.2 mL), and transferred to a preweighed vial. The product mixture was dried in vacuo to constant weight, and the crude yield was determined after subtracting out the catalyst weight (0.95 g, 32%). The product was dissolved in methylene chloride (3 mL) and precipitated from methanol (30 mL). The polymer was collected and dried in vacuo to constant weight, and the polymer yield was determined (0.91 g, 31%).

Acknowledgment. G.W.C. gratefully acknowledges a Packard Foundation Fellowship in Science and Engineering, and funding from the NSF (CHE-0243605), the Cornell Center for Materials Research (supported through the NSF MRSEC program, DMR-0079992), Sumitomo Chemicals, and the Cornell University Center for Biotechnology, a New York State Center for Advanced Technology.

JA051744L