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ARTICLE

Alternating Copolymerization of Cyclohexene Oxide with Carbon Dioxide Catalyzed by (salalen)CrCl Complexes

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ABSTRACT: Copolymerization of cyclohexene oxide with carbon dioxide was investigated by using chromium complexes with salalen ligands which are reduced analogues of salen ones (salen-H_2 = *N*,*N*′-disalicylidene-1,2-ethylenediamine). Although the use of (salalen)CrCl complexes alone without additives was not effective for the copolymerization, a mixture of (salalen)CrCl complexes and onium salts catalyzed the copolymerization with relatively high catalytic activity. Particularly, the present catalyst system showed the highest catalytic activity under atmospheric pressure of CO_2 among those ever reported. In general, the obtained copolymers consisted of almost perfectly alternating structure. Structural analysis of the copolymers by MALDI-TOF mass spectrometry revealed that chloride initiated the copolymerization. In addition, concomitant water was found to work as a chain transfer reagent and a bifunctional initiator.

Introduction

The alternating copolymerization of epoxides with CO_2, which was first reported by Inoue, Koinuma, and Tsuruta in 1969,[1] is one of the most promising processes for CO_2 utilization. Continuous research efforts have been devoted to the development of copolymerization catalysts during the past four decades, resulting in the significant improvement of the catalytic activity and selectivities (polycarbonates/cyclic carbonate ratio, carbonate/ether linkages ratio, regioselectivity, and stereoselectivity).[2] Particularly, in the past decade, some well-defined homogeneous metal complexes have been reported to be highly active and/or selective catalysts. The representatives are metal complexes with phenoxide,[3] β-diiminate,[4] and salen ligands (salen-H_2 = *N*,*N*′-disalicylidene-1,2-ethylenediamine).[5−7]

Metal−salen complexes are now used as catalysts in a variety of metal-catalyzed organic transformations.[8] A variety of diamines and salicylaldehydes are now commercially or synthetically available, and salen-H_2 can be synthesized via simple condensation of diamines with salicylaldehydes. Accordingly, it is relatively easy to evaluate the steric and electronic effects of salen ligands on the reactions systematically, which is advantageous for fine-tuning of catalyst systems. Recently, salalen and salan ligands, which are reduced analogues of salen ones, have been studied in some metal-catalyzed reactions.[8e] Because of their reduced structures, the electronic and steric factors of nitrogen donor are different from those of salen ligands. In addition, salalen and salan ligands are endowed with higher flexibility, resulting in higher tendency to form metal complexes with a *cis*-β configuration where nitrogen and oxygen donor atoms occupy three equatorial and one axial coordination sites of an octahedral geometry. This tendency is contrastive to that of salen ligands: metal complexes with a salen ligand generally occupy four equatorial coordination sites to form a *trans*-configuration. Such characteristics of salalen and salan ligands give unique reactivities to their metal complexes.

The effects of salen-ligand structure on the alternating copolymerization of epoxides with CO_2 have also been investigated, showing that subtle ligand modifications caused dramatic influences on activity and/or selectivities.[5e,g,h,6a,d−h,j,7] In addition, very recently, Lu and co-workers reported the copolymerization of epoxide with CO_2 by using chromium−salan complexes which showed higher catalytic performance (activity, polymer/cyclic carbonate ratio, regioselectivity, and stereoselectvity) than the corresponding chromium−salen complexes.[9] The authors proposed that such higher catalytic performance should be attributed to lower electrophilicity and larger steric bulk around the chromium center derived from sp^3-hybridized amino donors.

In the course of our investigation on the catalyst development for the epoxide/CO_2 alternating copolymerization, we have also been interested in using salalen or salan ligands to improve catalytic activity. Herein, we report the copolymerization by using chromium complexes with salalen ligands. We investigate the influence of the salalen structure on the activity and selectivities. The most interesting characteristic of the present catalyst system is that it demonstrates the highest catalytic activity under the atmospheric pressure of CO_2 among the catalyst systems ever reported.[10]

Results and Discussion

Syntheses of Salalen Ligands and Cr(salalen)Cl Complexes. To investigate the relationship between ligand structure and catalytic activity, we synthesized a variety of salalen ligands, especially focusing on the substituents on a nitrogen atom and the ethylene bridge of a diamine unit (Scheme 1). (Salalen-H_2)s **1a**-H_2−**1c**-H_2 with a hydrogen substituent on a nitrogen atom were synthesized via a similar procedure in the literature: monocondensation of a diamine or its hydrogen chloride salt with 3,5-di-*tert*-butylsalicylaldehyde (**6**), the following reduction by using $NaBH_4$, and the second condensation with salicylaldehyde **6**.[11] (Salalen-H_2)s **2a**-H_2, **2c**-H_2, **2d**-H_2, and **3**-H_2−**5**-H_2 with an alkyl or a phenyl group on a nitrogen atom were obtained via monocondensation of a diamine with salicylaldehyde **6** and the following nucleophilic substitution reaction with 2-bromomethyl-4,6-di-*tert*-butylphenol. The *N*-Me-type ligand precursor **2b**-H_2 was synthesized via the

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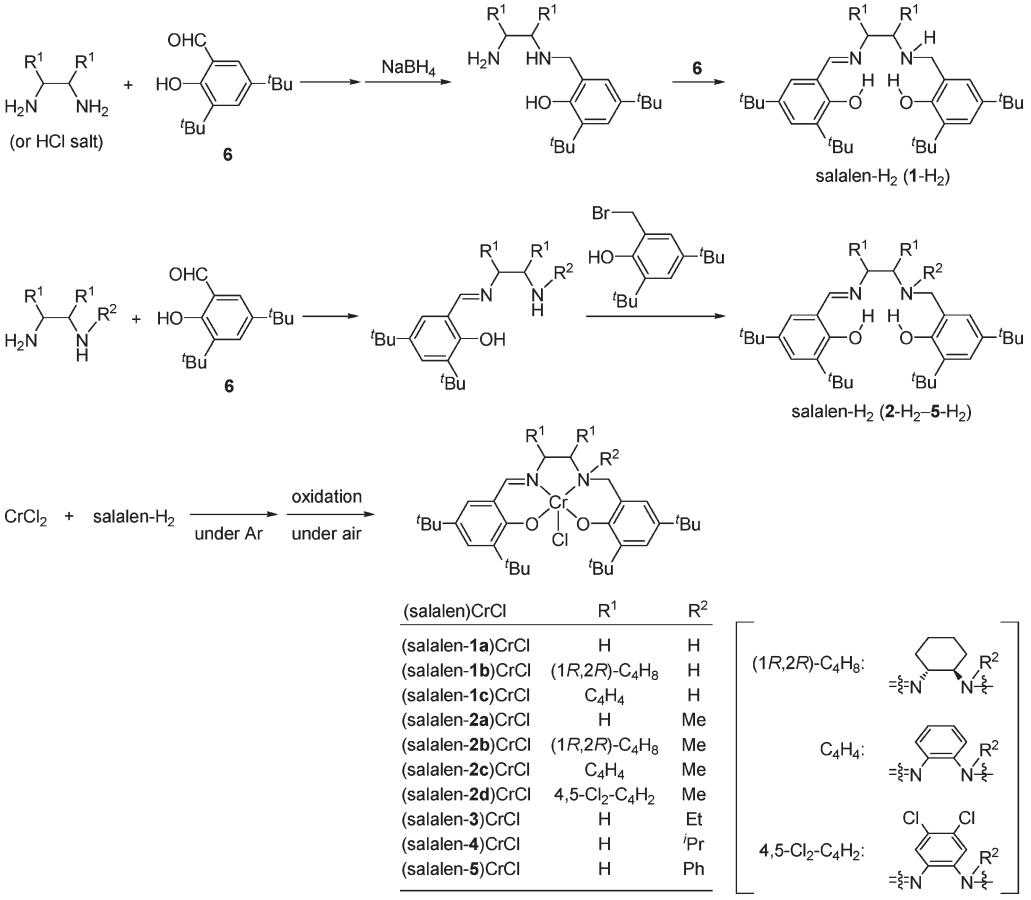
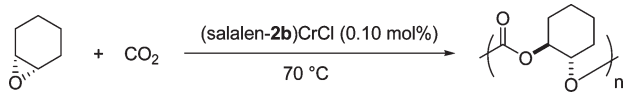
Scheme 1. General Synthetic Schemes for Salalen-H_2 and (salalen)CrCl Complexes



(salalen)CrCl	R^1	R^2
(salalen-**1a**)CrCl	H	H
(salalen-**1b**)CrCl	(1*R*,2*R*)-C_4H_8	H
(salalen-**1c**)CrCl	C_4H_4	H
(salalen-**2a**)CrCl	H	Me
(salalen-**2b**)CrCl	(1*R*,2*R*)-C_4H_8	Me
(salalen-**2c**)CrCl	C_4H_4	Me
(salalen-**2d**)CrCl	4,5-Cl_2-C_4H_2	Me
(salalen-**3**)CrCl	H	Et
(salalen-**4**)CrCl	H	^{i}Pr
(salalen-**5**)CrCl	H	Ph

Table 1. Copolymerization of CHO and CO_2 with (salalen)CrCl in the Presence of Cocatalyst[a]



entry	cocatalyst (equiv to Cr)	time (h)	yield (%)[b]	TOF (h^{-1})[c]	M_n[d] (g mol^{-1})	M_w/M_n[d]	carbonate linkage (%)[e]
1		19	trace				
2	[PPN]Cl (1)	3	52	170	10200	1.16	>99
3	[PPN]Cl (1)	2	37	190	9100	1.15	>99
4	[PPN]Cl (0.5)	2	13	65	3000	1.05	98
5	[PPN]Cl (2)	2	trace				
6	[PPN]N_3 (1)	3	51	170	11000	1.15	>99
7	[PPN]F (1)	3	51	170	6700	1.13	>99
8	Bu_4NCl (1)	3	trace				
9	**7**	7	trace				
10	Bu_4PCl (1)	3	trace				

[a] Copolymerization conditions: cyclohexene oxide (CHO, 1 mL, 1000 equiv to Cr), CO_2 (3.4 MPa for entry 1, 1.3 MPa for entries 2−10), (salalen-**2b**)CrCl, and cocatalyst (the amounts are shown in the Table) at 70 °C. [b] Isolated yield. In all cases, cyclic cyclohexene carbonate was not observed in the ^{1}H NMR spectrum of the reaction mixture. [c] Turnover frequency (TOF) = (mol of repeating unit)·(mol of Cr)$^{-1}$·h^{-1}. [d] Estimated by size-exclusion chromatography analysis using a polystyrene standards. [e] Calculated by ^{1}H NMR spectroscopy.

reported procedure.[12] The reaction of $CrCl_2$ with salalen-H_2 and the subsequent oxidation under air yielded the corresponding (salalen)CrCl complexes. Although suitable single crystals of the synthesized complexes for X-ray analysis were not obtained, the crystal structure of (salalen-**2b**)CrCl was reported by Katsuki and co-workers, where the salalen ligand adopts a *cis-β* structure.[13]

Alternating Copolymerization of Cyclohexene Oxide with Carbon Dioxide by Using (salalen)CrCl and Cocatalysts. The copolymerization of cyclohexene oxide (CHO) with CO_2 was carried out by using (salalen)CrCl complexes at 70 °C (Table 1).[14] Although almost negligible activity was observed in the absence of cocatalyst (entry 1), the addition of cocatalyst [PPN]Cl ([PPN]$^+$ = bis(triphenylphosphoranylidene)iminium) resulted in production of the alternating copolymer (entry 2). These results indicate that the chromate complexes derived from (salalen)CrCl and onium salt should be the active species.[5d,f,g,15] The obtained copolymers possessed the almost-perfectly alternating structure based on the ^{1}H NMR spectrum. A possible byproduct, cyclohexene carbonate, was not detected. Optimization of the molar ratio between chromium complexes and [PPN]Cl revealed that the highest activity was achieved

Table 2. Effect of Ligand Structure on Copolymerization of CHO with CO_2[a]

entry	Cr complex	yield (%)[b]	TOF (h^{-1})[c]	M_n[d] (g mol^{-1})	M_w/M_n[d]	carbonate linkage (%)[e]
1	(salalen-**2a**)CrCl	42	140	6600	1.13	99
2	(salalen-**2b**)CrCl	52	170	10200	1.16	>99
3	(salalen-**2c**)CrCl	50	170	5300	1.11	98
4	(salalen-**2d**)CrCl	50	170	10900	1.17	>99
5	(salalen-**1a**)CrCl	15[e]	51[e]	3300	1.07	97
6	(salalen-**1b**)CrCl	28	94	6900	1.14	99
7	(salalen-**1c**)CrCl	28	91	6000	1.10	99
8	(salalen-**3**)CrCl	32	110	7600	1.12	99
9	(salalen-**4**)CrCl	19[e]	62[e]	3900	1.08	98
10	(salalen-**5**)CrCl	trace				

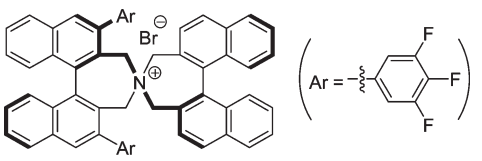
[a] Copolymerization conditions: cyclohexene oxide (CHO, 1 mL, 1000 equiv to Cr), CO_2 (1.3 MPa), (salalen)CrCl, and cocatalyst (1.0 equiv to Cr) at 70 °C for 3 h. [b] Isolated yield. In all cases, cyclic cyclohexene carbonate was not observed in the ^{1}H NMR spectrum of the reaction mixture. [c] Turnover frequency (TOF) = (mol of repeating unit)·(mol of Cr)$^{-1}$·h^{-1}. [d] Estimated by size-exclusion chromatography analysis using a polystyrene standards. [e] Calculated by ^{1}H NMR spectroscopy.

Table 3. Effect of CO_2 Pressure on the Copolymerization of CHO and CO_2[a]

entry	Cr complex	time (h)	P_{CO_2} (MPa)	yield (%)[b]	TOF (h^{-1})[c]	M_n[d] (g mol^{-1})	M_w/M_n[d]	carbonate linkage (%)[e]
1	(salalen-**2b**)CrCl	2	0.1	20	100	5200	1.10	98
2		5	0.1	47	100	8700	1.15	99
3		2	0.6	32	160	7000	1.15	>99
4		2	1.3	43	210	8800	1.14	>99
5		2	3.4	46	230	9100	1.15	>99
6		2	5.2	17	83	5300	1.07	99
7	(salph)CrCl	5	0.1	26	50	6400	1.13	98
8	(salcy)Co($OBzF_5$)	5	0.1	1	2			>99

[a] Copolymerization conditions: cyclohexene oxide (CHO, 1 mL, 1000 equiv to Cr or Co), CO_2, Cr or Co complex, and cocatalyst (1.0 equiv to Cr or Co) at 70 °C. [b] Isolated yield. In all cases, cyclic cyclohexene carbonate was not observed in the ^{1}H NMR spectrum of the reaction mixture. [c] Turnover frequency (TOF) = (mol of repeating unit)·(mol of Cr or Co)$^{-1}$·h^{-1}. [d] Estimated by size-exclusion chromatography analysis using a polystyrene standards. [e] Calculated by ^{1}H NMR spectroscopy.

when using 1 equiv of [PPN]Cl (entries 3−5). Other counteranions for $[PPN]^+$, such as azide and fluoride, can be also employable without a significant influence on catalytic activity (entries 6 and 7). In contrast to [PPN]X (X = F, Cl, N_3), Bu_4NCl, chiral ammonium salt **7**,[16] and Bu_4PCl did not work as good cocatalysts (entries 8−10). A similar trend was also reported for the copolymerization with cobalt−salen complxes in the previous literatures, where [PPN]X (X = halide, benzoate, azide) worked as better cocatalysts than R_4NX (X = halide).[6e,g] In these literatures, it was proposed that the bulkiness and the ability in delocalizing positive charge should be required for the cation moiety of cocatalysts to achieve higher catalytic activity.



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Next, we examined the copolymerization by using various types of chromium complexes as shown in Table 2. Salalen ligands **2b** and **2c** with cyclohexanediamine unit and phenylenediamine unit, respectively, gave the comparable catalytic activity with each other (entries 2 and 3) and the higher activity than the corresponding ligand **2a** derived from ethylenediamine (entry 1). The same trend was also observed when using ligands **1** with a hydrogen substituent on a nitrogen atom (entries 5−7). Introduction of chloro substituents on a phenylenediamine moiety did not give any influence (entry 4). Each of *N*-H-type salalen ligand **1** caused lower catalytic activity than the corresponding *N*-Me-type salalen ligand **2** (entries 1−3 and 5−7). The complexes with sterically more hindered salalen ligands **3**−**5** also showed lower catalytic activity than (salalen-**2a**)CrCl (entries 1 and 8−10). As a substituent on the nitrogen atom, methyl group was found to be most favorable for higher catalytic activity.[17,18] Electronic and steric factors may explain such substituent effects on the catalytic activity. In the previous literature, chromium−salan complexes demonstrated higher catalytic activity in the copolymerization of propylene oxide with CO_2 than chromium−salen complexes.[9] The higher catalytic activity was proposed to be attributed to higher electron-donating ability of salan ligands than that of salen ligands. Accordingly, *N*-Me-type salalen ligands **2** showed higher catalytic activity than *N*-H-type salalen ligands **1**. Nevertheless, steric bulk on the nitrogen atom in salalen ligands **3**−**5** may hinder the access of monomers, leading to lower catalytic activity.

The present catalyst system kept its activity under low CO_2 pressure. As shown in Table 3, the pressure dependence of the copolymerization was investigated by employing an equimolar mixture of (salalen-**2b**)CrCl and [PPN]Cl. An increase in CO_2 pressure from 0.1 MPa (entry 1) to 3.4 MPa (enrty 5) resulted in acceleration in the reaction rate. However, further increase to 5.2 MPa gave negative effect on catalytic activity (entry 6). According to the report by Darensbourg and co-workers, an increase in catalytic activity along with an increase in CO_2 pressure (up to 3.4 MPa) indicates that CO_2 insertion is significantly related to the determination of the copolymerization rate at <3.4 MPa.[19] On the other hand, a decrease in catalytic activity under higher CO_2 pressure is attributed to the dilution effect of CO_2 on the concentrations of catalyst and epoxide.[19,20] The noteworthy feature of the present catalyst system is that the high catalytic activity (TOF = 100 h^{-1}) was held even under atmospheric CO_2 pressure. In addition, despite such low CO_2 pressure, the almost-perfectly alternating copolymers were obtained. Successful production of the almost-perfectly alternating copolymers under 0.1 MPa of CO_2 is contrastive to other catalyst systems ever reported. To the best of our knowledge, there have been only a few reports on the copolymerization under atmospheric CO_2 pressure,

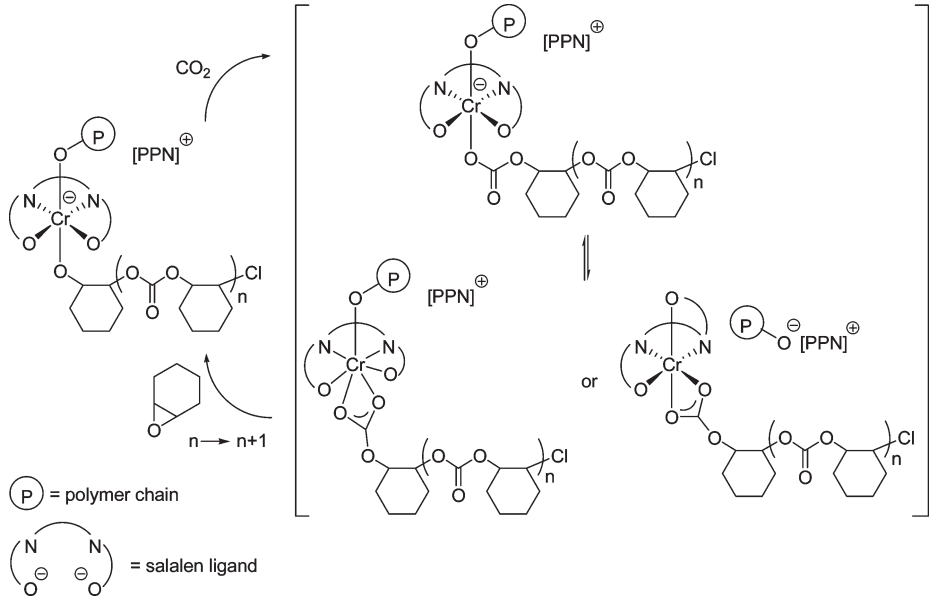

Figure 1. Plausible reaction sequence for the copolymerization of CHO with CO_2 by using (salalen)CrCl: a bidentate-binding mode of a carbonate chain end on the assumption that the chromium center forms a seven- or six-coordinate configuration.

where the catalytic activities of TOF were below 25 h^{-1}.[19,21] We also confirmed that the reported chromium−salen and cobalt−salen complexes [(salph)CrCl (salph-H_2 = *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine); (salcy)Co($OBzF_5$) (salcy-H_2 = (1*R*,2*R*)-*trans*-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, $OBzF_5$ = OC(=O)C_6F_5)], which are highly active under CO_2-pressurized conditions, showed much lower catalytic activity than the present (salalen-**2b**)CrCl complex (entries 7 and 8). Accordingly, the present system can be ranked as the most active catalyst under atmospheric CO_2 pressure.[10]

We propose that the flexibility of the salalen ligand would be responsible for the high catalytic performance (activity and carbonate-linkage content) of chromium−salalen complex under atmospheric CO_2 pressure. When catalyzed by a mixture of a chromium− or cobalt−salen complex and an onium salt, the copolymerization is proposed to proceed via the alternating CO_2 insertion into metal−alkoxide bond and the epoxide insertion into metal−carbonate bond in a six-coordinate anionic metal species (Figure 1). Under low CO_2 pressure, low-barrier CO_2 insertion and/or high resistance to decarboxylation would be essential for the high catalytic performance. The carbonate chain end can be bound to the chromium center in monodentate- and bidentate-binding mode. Considering (i) that a bidentate binding is calculated to be more favorable than a monodentate one in some metal−carboxylate complexes[22] and (ii) that a favorable bidentate-binding mode of an acetate ligand was observed in the cobalt complexes with a salpn ligand (salpn-H_2 = *N,N′*-disalicylidene-1,3-diaminopropane), which is flexible than salen ligand,[23] the bidentate-binding mode would be more favorable to the carbonate chain end, resulting in stabilization of metal−carbonate species. Thus, it would be advantageous to low-energy CO_2 insertion and high resistance to decarboxylation that a metal complex can easily accept such a bidentate-carbonate chain end. In a previous literature, a bidentate binding mode of zwitterionic carbamic ligand to chromium center was observed after the reaction of (salen)CrN_3 with 4-(*N,N*-dimethylamino)pyridine and CO_2.[5f] It was not mentioned clearly whether the resulting chromium complex formed a heptacoordinate configuration or a six-coordinate configuration via dissociation of one of nitrogen, oxygen, and axial donors. In either case, the acceptance of a bidentate-carbonate chain end, which requires two *cis*-coordination sites, would impose a conformational change on the chromium−salen complex which favors to form *trans*-configuration. As mentioned above, salalen ligands are more flexible than salen ligands. Accordingly, the chromium−salalen complex should adopt a bidentate binding mode of a carbonate chain end more easily than the chromium−salen complex during the copolymerization (Figure 1), resulting in the high catalytic performance under low CO_2 pressure.

The calculation results by Rieger and co-workers also indicate that the flexibility of the salalen ligand may be favorable to the CO_2 insertion step. The CO_2 insertion into a chromium−alkoxide bond in a six-coordinate chromium−salen complex was reported to require an open coordination site.[24] Such a coordination site was provided via decoordinative rotation of one of the phenoxy-oxygen atoms of the salen ligand, with activation barrier of +100 kJ mol^{-1}. Chromium−salalen complexes would undergo such decoordinative rotation more easily because of the flexibility of the salalen ligands, leading to lower-barrier CO_2 insertion.

Structural Analyses of the Copolymers. Stereoselective copolymerization of CHO with CO_2 was first reported by using zinc complexes with enantiomerically pure aminoalkoxido ligands or imine−oxazoline ligands to give optically active copolymers enriched with *meso*-centered tetrad.[25] Cobalt−chiral salen complexes also achieve the stereoselective copolymerization, producing the copolymers enriched with *meso*-centered or *racemo*-centered tetrad depending on the ligand structure and whether an additive is added.[6f,h] In contrast, there has been no report on stereoselective copolymerization of CHO with CO_2 by using chromium−salen complexes.[5a] As mentioned above, salen ligands generally coordinate to metal centers in *trans*-fashion, while salalen ones tend to coordinate in *cis*-β fashion. Thus, we expected that such unique coordination mode of salalen ligands leads their chromium complexes to achieve stereoselective copolymerization. Indeed, chromium−salan complexes achieved the enantioselective copolymerization of propylene oxide with CO_2, although the structure of the complexes was unclear. Figure 2 shows the carbonyl region of ^{13}C NMR

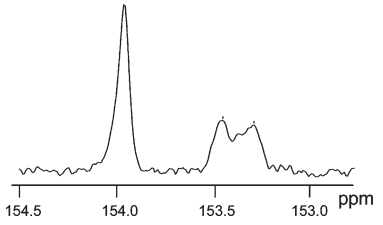

Figure 2. Carbonyl region of ^{13}C NMR spectrum of the copolymer (Table 3, entry 4).

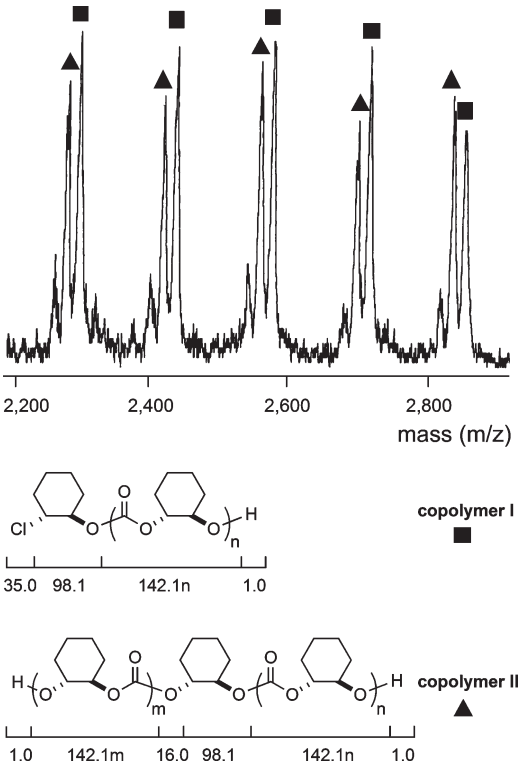

Figure 3. MALDI-TOF MS spectrum of the copolymer (Table 3, entry 4).

spectrum of the copolymer obtained by using (salalen-**2b**)CrCl (Table 3, entry 4). On the basis of the assignment in previous literatures,[6f,25,26] the spectrum indicates the formation of almost atactic copolymer. The copolymers produced by using other salalen ligands also showed similar spectra. Nevertheless, we measured the degree of asymmetric induction during the copolymerization with (salalen-**2b**)CrCl because salalen ligand **2b** is derived from optically pure (1*R*,2*R*)-cyclohexanediamine. Alkali treatment of the copolymer obtained with (salalen-**2b**)CrCl gave *trans*-cyclohexane-1,2-diol with enantiomeric excess of 11% (*R*,*R*),[25,27] which indicates that (salalen-**2b**)CrCl complex achieved the low degree of desymmetrization in epoxide-ring-opening step. The degree is too low to be reflected in the ^{13}C NMR spectrum.

Identification of terminal groups of the resulting copolymers was also conducted. As shown in Figure 3 and Figure S17, the MALDI-TOF MS spectrum of the copolymer showed the two series of signals with the regular interval of 142.2 m/z as main series. The mass numbers of one series correspond [142.1n (repeating unit) + 35.0 (Cl) + 98.1 (CHO) + 1.0 (H) + 23.0 (Na^+ ion)]. As one can easily anticipate, this result demonstrates that the chloride from (salalen-**2b**)CrCl and/or [PPN]Cl worked as initiators to produce the copolymer **I**. On the other hand, the mass number of another series matches [142.1(m + n) (repeating unit) + 18.0 (H_2O) + 98.1 (CHO) + 23.0 (Na^+ ion)]. According to the literatures, the copolymer **II** should be produced via the chain-transfer reaction by contaminant water.[7,28] This is why the peak profiles of SEC of the resulting copolymers were bimodal and the number-average molecular weights of the copolymers were smaller than the theoretical value calculated from the copolymer yield and the total molar amount of chloride. In spite of such a chain-transfer reaction, molecular-weight distribution was relatively narrow, indicating that the copolymerization proceeded via an immortal fashion with reversible and rapid chain-transfer reaction.[7,28,29]

Conclusion

Copolymerization of cyclohexene oxide with carbon dioxide was investigated by using several chromium complexes with a salalen ligand. When using a mixture of (salalen)CrCl complex and [PPN]Cl, the copolymerization gave poly(cyclohexene carbonate) selectively. This catalyst system was found to produce the almost-perfectly alternating copolymer under low pressure of CO_2. In particular, the (salalen-**2b**)CrCl complex showed the highest catalytic activity under atmospheric pressure of CO_2 (TOF = 100 h^{-1}) among the reported catalyst systems. Although the degree was not extremely high, asymmetric induction was observed. On the basis of the structural analysis of the obtained copolymers, the copolymerization was indicated to proceed in an immortal fashion.

Experimental Section

General Methods. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glovebox under argon atmosphere or with the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns. Most of reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25 mm 230−400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). For a silica gel column chromatography, Silica gel 60N (spherical neutral, particle size 63-210 μm, Kanto Kagaku Co., Ltd.) was used. NMR spectra were recorded in deuteriochloroform on a 500 MHz (^1H 500 MHz; ^{13}C 125 MHz) or 400 MHz (^1H 400 MHz; ^{13}C 100 MHz) spectrometer. Chemical shifts are reported in ppm relative to the residual protiated solvent peak (7.26 ppm for $CHCl_3$) for ^1H and deuteriochloroform (77.16 ppm) for ^{13}C. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on a melting point apparatus. The recycling preparative SEC was performed with a JAI GEL-1H and -2H columns (chloroform as an eluent). High-resolution mass spectra were taken with FAB method. Size-exclusion chromatography (SEC) analyses were carried out using two columns (Shodex KF-804 L) using tetrahydrofuran as an eluent at 40 °C at 1 mL/min. The molecular weight was calibrated against standard polystyrene samples. 2-Bromomethyl-4,6-di-*tert*-butylphenol,[30] *N*-methyl-4,5-dichloro-1,2-diaminnobenzene,[31] and **2b-H$_2$**[12] were synthesized according to the reported procedures.

Synthesis of Salalen 1a-H$_2$. To a solution of ethylenediamine (1.32 g, 22.0 mmol) in dry CH_2Cl_2 (2.0 mL) in a 100 mL flask, a solution of 3,5-di-*tert*-butylsalicylaldehyde (500 mg, 2.1 mmol) in dry CH_2Cl_2 was added dropwise. After the mixture was

stirred at room temperature for 10 min, the solvent and excess ethylenediamine were removed in vacuo. The residue was dissolved with anhydrous MeOH (11 mL). Sodium borohydride ($NaBH_4$, 808 mg, 21.3 mmol) was slowly added and stirred at room temperature for 2.5 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was dissolved with dry hexane and cooled to −30 °C. The resulting light yellow solid was collected by filtration and dried in vacuo to give the title compound **1a**-H_2 as a pale-yellow solid (118 mg, 22%); mp 172.6−174.1 °C. ^{1}H NMR ($CDCl_3$): δ 13.44 (br, 1H), 8.43 (s, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.23 (d, J = 2.4 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H), 4.00 (s, 2H), 3.78 (t, J = 5.5 Hz, 2H), 3.05 (t, J = 5.5 Hz, 2H), 1.45 (s, 9H), 1.42 (s, 9H), 1.31 (s, 9H), 1.28 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 167.9, 158.0, 154.7, 140.7, 140.4, 136.8, 136.1, 127.4, 126.2, 123.4, 123.2, 121.8, 117.8, 59.3, 53.3, 48.6, 35.2, 35.1, 34.3, 31.8, 31.6, 29.8, 29.6. One signal derived from ^{t}Bu group in ^{13}C NMR spectrum was missing because of overlap. Anal. Calcd for $C_{32}H_{50}N_2O_2$ (%): C, 77.68; H, 10.19; N, 5.66. Found: C, 77.65; H, 10.23; N, 5.79.

Synthesis of Salalen 1b-H_2. To a solution of (*R*,*R*)-1,2-cyclohexanediamine mono(hydrogen chloride) (367 mg, 2.4 mmol) in dry MeOH (3.0 mL), the solution of 3,5-di-*tert*-butylsalicylaldehyde (582 mg, 2.5 mmol) in dry MeOH (8.0 mL) was added. The resulting yellow solution was stirred at room temperature for 19 h and was concentrated in vacuo. The obtained yellow residue was dissolved with dry MeOH (ca. 30 mL), and $NaBH_4$ (474 mg, 11.3 mmol) was added in small portions at 0 °C. After stirring at room temperature for 2 h, the reaction mixture was quenched by adding water and extracted with Et_2O (3 × 15 mL). The organic phase was washed with brine (3 × 15 mL), dried with Na_2SO_4, and concentrated under reduced pressure. The crude residue was used for the next step without further purification.

The crude residue was dissolved with MeOH (20 mL), and 3,5-di-*tert*-butylsalicylaldehyde (531 mg, 2.24 mmol) was added. After stirring at ambient temperature for 18 h, the resulting light yellow precipitate was filtrated, washed with cold MeOH, and dried in vacuo to give the title compound **1b**-H_2 a pale-yellow solid (918 mg, 69%); mp 151.5−154.9 °C. ^{1}H NMR ($CDCl_3$): δ 13.48 (s, 1H), 10.81 (br, 1H), 8.41 (s, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 4.04 (d, J = 13.4 Hz, 1H), 3.81 (d, J = 13.4 Hz, 1H), 3.06−3.01 (m, 1H), 2.83−2.78 (m, 1H), 2.27−2.22 (m, 1H), 1.86−1.65 (m, 5H), 1.44 (s, 9H), 1.42−1.35 (m, 2H), 1.34 (s, 9H), 1.28 (s, 9H), 1.24 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 166.7, 158.1, 154.6, 140.6, 140.4, 136.7, 136.1, 127.3, 126.2, 123.2, 123.0, 122.9, 117.9, 73.9, 61.3, 50.9, 35.2, 35.0, 34.3, 34.2, 31.8, 31.6, 30.5, 29.8, 29.7, 24.8, 24.6. One signal derived from ^{t}Bu group in ^{13}C NMR spectrum was missing because of overlap. Anal. Calcd for $C_{36}H_{56}N_2O_2$ (%): C, 78.78; H, 10.28; N, 5.10. Found: C, 78.76; H, 10.24; N, 5.36.

Synthesis of Salalen 1c-H_2. A 50 mL round-bottom flask was charged with 1,2-phenylenediamine (208 mg, 1.9 mmol), and the solution of 3,5-di-*tert*-butylsalicylaldehyde (410 mg, 1.7 mmol) in dry MeOH (6.0 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature, and the yellow precipitate was observed. To the reaction mixture was added $NaBH_4$ (323 mg, 7.7 mmol) in small portions. After stirring at room temperature for 5 h, the reaction mixture was quenched by adding water and extracted with Et_2O (3 × 20 mL). The organic phase was washed with brine (3 × 20 mL), dried with Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (hexane/AcOEt = 5/1) to give a white solid.

The obtained white solid was dissolved with MeOH (10 mL), and 3,5-di-*tert*-butylsalicylaldehyde (389 mg, 1.64 mmol) was added. After stirring overnight at 70 °C, the resulting precipitate was filtrated and washed with cold MeOH. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 5/1), and the further purification by recrystallization from CH_2Cl_2/hexane gave the title compound **1c**-H_2 as a yellow solid (234 mg, 25%); mp 143.6−145.6 °C. ^{1}H NMR ($CDCl_3$): δ 12.93 (s, 1H), 8.60 (s, 1H), 8.44 (br, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.28 (d, J = 2.4 Hz, 1H), 7.25−7.21 (m, 2H), 7.08−6.94 (m, 4H), 4.46 (s, 2H), 1.43 (s, 9H), 1.42 (s, 9H), 1.32 (s, 9H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.3, 158.0, 153.5, 141.7, 141.0, 138.7, 137.2, 136.7, 128.6, 127.9, 127.1, 123.8, 123.7, 122.2, 121.0, 118.8, 118.6, 114.7, 49.7, 35.3, 35.1, 34.40, 34.36, 31.8, 31.6, 29.9, 29.6. One signal derived from aromatic carbon in ^{13}C NMR spectrum was missing because of overlap. Anal. Calcd for $C_{36}H_{50}N_2O_2$ (%): C, 79.66; H, 9.28; N, 5.16. Found: C, 79.82; H, 9.27; N, 5.41.

Synthesis of Salalen 2a-H_2. A 20 mL Schlenk tube was charged with 3,5-di-*tert*-butylsalicylaldehyde (318 mg, 1.3 mmol) and anhydrous MeOH (3.0 mL). *N*-Methylethylenediamine (186 mg, 2.5 mmol) was added, and the resulting mixture was stirred overnight at room temperature under Ar. The solvent and the remaining diamine were removed off in vacuo at 40 °C to give a yellow viscous liquid which was used for the next step without further purification.

The yellow oil and 2-bromomethyl-4,6-di-*tert*-butylphenol (402 mg, 1.3 mmol) were dissolved in dry THF (3.0 mL) under Ar. To the mixture was added a solution of triethylamine (0.20 mL) in dry THF (1 mL). After stirring at ambient temperature for 4 h in the dark, the resulting white precipitate was removed off by filtration. The filtrate was concentrated under reduced pressure, and the resulting crude residue was dissolved with a minimum amount of dry hexane and cooled to −30 °C to give the title compound **2a**-H_2 as a light-yellow solid (569 mg, 84% for two steps). Spectral data was identical to the reported ones.[32]

Synthesis of Salalen 2c-H_2. A 20 mL Schlenk was charged with 3,5-di-*tert*-butylsalicylaldehyde (693 mg, 2.9 mmol) and anhydrous MeOH (9.0 mL). To the solution was added *N*-methyl-1,2-phenylenediamine (0.40 mL, 3.4 mmol). The resulting mixture was stirred overnight with refluxing under Ar and cooled to 0 °C. The resulting precipitate was collected by filtration and dried in vacuo to give a crude condensation product (922 mg, 2.7 mmol) which was used for the next step without further purification.

The second step was conducted by using a part of the crude condensation product (274 mg, 0.81 mmol) and bromomethyl-4,6-di-*tert*-butylphenol (246 mg, 0.81 mmol) according to the procedure for **2a**-H_2. The crude residue was dissolved with a minimum amount of dry MeOH and cooled to −30 °C to give the title compound **2c**-H_2 as a yellow solid (317 mg, 65% for two steps); mp 118.6−120.6 °C. ^{1}H NMR ($CDCl_3$): δ 13.00 (s, 1H), 10.10 (s, 1H), 8.62 (s, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.32−7.27 (m, 2H), 7.25 (d, J = 2.4 Hz, 1H), 7.23−7.18 (m, 2H), 7.11−7.07 (m, 1H), 6.95 (d, J = 1.8 Hz, 1H), 4.31 (s, 2H), 2.69 (s, 3H), 1.46 (s, 9H), 1.38 (s, 9H), 1.34 (s, 9H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.4, 158.3, 154.2, 145.4, 145.2, 140.7, 140.6, 137.3, 136.0, 128.5, 127.2, 125.6, 123.8, 123.3, 121.1, 120.9, 120.5, 118.6, 59.9, 43.0, 35.3, 35.1, 34.35, 34.31, 31.9, 31.6, 29.9, 29.6. One signal derived from aromatic carbon in ^{13}C NMR spectrum was missing because of overlap. Anal. Calcd for $C_{37}H_{52}N_2O_2$ (%): C, 79.81; H, 9.41; N, 5.03. Found: C, 79.74; H, 9.39; N, 5.24.

Synthesis of Salalen 2d-H_2. A 100 mL flask was charged with *N*-methyl-4,5-dichloro-1,2-diaminobenzene (232 mg, 1.21 mmol), 3,5-di-*tert*-butylsalicylaldehyde (288 mg, 1.21 mmol), and anhydrous MeOH (7 mL). The resulting solution was stirred overnight at room temperature. After a few drops of formic acid were added, the solution was further stirred overnight at 80 °C. The reaction mixture was filtrated off to remove the precipitate and concentrated under reduced pressure, affording a crude condensation product which was used for the next step without further purification.

The second step was conducted by using the crude condensation product and bromomethyl-4,6-di-*tert*-butylphenol (178 mg,

0.59 mmol) according to the procedure for **2a**-H_2. The crude product was purified by the recycling preperative SEC to give the title compoumd **2d**-H_2 as a yellow solid (262 mg, 35% for two steps). ^{1}H NMR ($CDCl_3$): δ 12.64 (s, 1H), 9.41 (s, 1H), 8.57 (s, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.34 (s, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 2.4 Hz, 1H), 7.16 (s, 1H), 6.94 (d, J = 2.4 Hz, 1H), 4.26 (s, 2H), 2.69 (s, 3H), 1.45 (s, 9H), 1.37 (s, 9H), 1.34 (s, 9H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 166.2, 158.4, 153.8, 144.8, 144.4, 141.1, 141.0, 137.5, 136.3, 130.1, 129.3, 128.8, 127.5, 124.1, 123.6, 123.3, 121.7, 120.3, 118.2, 59.6, 42.9, 35.3, 35.1, 34.4, 34.3, 31.8, 31.6, 29.9, 29.6. Anal. Calcd for $C_{37}H_{50}Cl_2N_2O_2$ (%): C, 71.02; H, 8.05; N, 4.48. Found: C, 71.09; H, 8.01; N, 4.65.

Synthesis of Salalen 3-H_2. The first and second steps were conducted by using 3,5-di-*tert*-butylsalicylaldehyde (341 mg, 1.4 mmol), *N*-ethylethylenediamine (156 mg, 1.7 mmol), and 2-bromomethyl-4,6-di-*tert*-butylphenol (430 mg, 1.4 mmol) according to the procedure for **2a**-H_2. The crude product was purified by the recycling preperative SEC to give the title compound **3**-H_2 as a pale-yellow solid (396 mg, 53%); mp. ^{1}H NMR ($CDCl_3$): δ 13.60 (s, 1H), 10.97 (br, 1H), 8.37 (s, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 6.84 (d, J = 2.1 Hz, 1H), 3.82 (s, 2H), 3.76 (t, J = 6.6 Hz, 2H), 2.90 (t, J = 6.6 Hz, 2H), 2.69 (q, J = 7.2 Hz, 2H), 1.44 (s, 9H), 1.39 (s, 9H), 1.31 (s, 9H), 1.28 (s, 9H), 1.11 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.5, 158.1, 154.5, 140.5, 140.2, 136.7, 135.7, 127.1, 126.1, 123.4, 123.0, 121.2, 118.0, 58.8, 57.5, 53.6, 47.8, 35.2, 35.0, 34.3, 31.9, 31.7, 29.7, 29.6, 11.4. One signal derived from quaternary carbon of ^{t}Bu group in the ^{13}C NMR spectrum was missing because of overlap. Anal. Calcd for $C_{34}H_{54}N_2O_2$ (%): C, 78.11; H, 10.41; N, 5.36. Found: C, 78.38; H, 10.55; N, 5.41.

Synthesis of Salalen 4-H_2. The first and second steps were conducted by using 3,5-di-*tert*-butylsalicylaldehyde (381 mg, 1.61 mmol), *N*-isopropylethylenediamine (199 mg, 1.91 mmol), and 2-bromomethyl-4,6-di-*tert*-butylphenol (481 mg, 1.61 mmol) according to the procedure for **2a**-H_2. The crude product was purified by reprecipitation from a minimum amount of dry hexane at −30 °C to give the title compound **4**-H_2 as a light-yellow solid (516 mg, 60%); mp 107.6−109.8 °C. ^{1}H NMR ($CDCl_3$): δ 13.66 (br, 1H), 11.12 (br, 1H), 8.36 (s, 1H), 7.37 (d, J = 2.1 Hz, 1H), 7.20 (d, J = 2.1 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 6.84 (d, J = 2.1 Hz, 1H), 3.85 (s, 2H), 3.72 (t, J = 6.4 Hz, 2H), 3.08 (sep, J = 6.7 Hz, 1H), 2.83 (br, 2H), 1.44 (s, 9H), 1.39 (s, 9H), 1.31 (s, 9H), 1.29 (s, 9H), 1.07 (d, J = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 167.6, 158.1, 154.7, 140.5, 140.1, 136.7, 135.7, 127.0, 126.1, 123.4, 122.9, 121.3, 118.0, 58.6, 55.5, 50.3, 49.7, 35.2, 35.0, 34.30, 34.28, 31.9, 31.7, 29.7, 29.6, 17.4. Anal. Calcd for $C_{35}H_{56}N_2O_2$ (%): C, 78.31; H, 10.51; N, 5.22. Found: C, 78.05; H, 10.48; N, 5.20.

Synthesis of Salalen 5-H_2. A 20 mL Schlenk tube was charged with 3,5-di-*tert*-butylsalicylaldehyde (363 mg, 1.5 mmol) and anhydrous MeOH (4.0 mL). After *N*-phenylethylenediamine (248 mg, 1.8 mmol) was added, the resulting solution was stirred overnight at room temperature under Ar and concentrated under reduced pressure. The crude residue was dissolved in hexane/AcOEt (3/1) and passed through a short pad of silica gel column chromatography to give a condensation product (54 mg).

The second step was conducted by using the condensation product and 2-bromomethyl-4,6-di-*tert*-butylphenol (495 mg, 1.7 mmol) according to the procedure for **2a**-H_2. The crude product was recrystallized with dry CH_2Cl_2 and dry hexane at −30 °C to give the title compound **5**-H_2 as a light-yellow solid (617 mg, 71%); mp 130.4−131.4 °C. ^{1}H NMR ($CDCl_3$): δ 13.49 (br, 1H), 9.08 (br, 1H), 8.16 (s, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.33 (t, J = 7.9 Hz, 2H), 7.24 (d, J = 2.1 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 4.41 (s, 2H), 3.66 (t, J = 6.6 Hz, 2H), 3.51 (t, J = 6.6 Hz, 2H), 1.45 (s, 9H), 1.40 (s, 9H), 1.30 (s, 9H), 1.28 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 167.6, 158.0, 153.8, 149.0, 141.4, 140.2, 136.8, 136.0, 129.5, 127.2, 126.0, 124.1, 123.5, 123.2, 121.3, 120.8, 117.9, 57.7, 56.7, 52.6, 35.2, 35.0, 34.4, 34.3, 31.8, 31.7, 29.8, 29.6. Anal. Calcd for $C_{38}H_{54}N_2O_2$ (%): C, 79.95; H, 9.53; N, 4.91. Found: C, 79.75; H, 9.75; N, 4.90.

General Synthesis of (salalen)CrCl Complexes. The chromium complexes were synthesized according to the reported procedure for synthesizing chromium−salen complexes.[5e] The salalen ligand precursor (1.0 equiv) and anhydrous $CrCl_2$ (1.1 equiv) were dissolved in THF and stirred under Ar at room temperature for 24 h. After the reaction mixture was exposed to air and stirred for an additional 24 h, it was diluted with Et_2O. The organic layer was washed with aqueous saturated NH_4Cl and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give chromium complex as a solid.

(salalen-1a)CrCl. The title complex was obtained from **1a**-H_2 and $CrCl_2$ as a dark-green solid. IR (cm^{-1}): 3198, 2954, 2868, 1624, 1533, 1462, 1441, 1414, 1362, 1256, 1202, 1169, 876, 839, 748, 550. HRMS-FAB$^+$ (m/z) calcd for $C_{32}H_{48}N_2O_2Cr$ $[M-Cl]^+$ 544.3121; found 544.3115. Anal. Calcd for $C_{32}H_{50}ClN_2O_3Cr$ [(salalen-**1a**)CrCl(H_2O)] (%): C, 64.25; H, 8.42; N, 4.68. Found: C, 62.55; H, 8.38; N, 4.64.

(salalen-1b)CrCl. The title complex was obtained from **1b**-H_2 and $CrCl_2$ as a dark-green solid. IR (cm^{-1}): 3186, 2953, 2866, 1620, 1533, 1464, 1437, 1412, 1387, 1362, 1254, 1202, 1169, 874, 837, 783, 748, 563, 544. HRMS-FAB$^+$ (m/z) calcd for $C_{36}H_{54}N_2O_2Cr$ $[M-Cl]^+$ 598.3590, found 598.3565. Anal. Calcd for $C_{36}H_{56}ClN_2O_3Cr$ [(salalen-**1b**)CrCl(H_2O)] (%): C, 66.29; H, 8.65; N, 4.29. Found: C, 65.48; H, 8.65; N, 4.32.

(salalen-1c)CrCl. The title complex was obtained from **1c**-H_2 and $CrCl_2$ as a red-brown solid. IR (cm^{-1}): 2955, 2868, 1611, 1585, 1528, 1462, 1421, 1389, 1360, 1256, 1200, 1163, 1109, 1024, 872, 837, 787, 752, 538. Anal. Calcd for $C_{36}H_{48}ClN_2O_2Cr$ [(salalen-**1c**)CrCl] (%): C, 68.83; H, 7.70; N, 4.46. Found: C, 70.19; H, 8.35; N, 4.32.

(salalen-2a)CrCl. The title complex was obtained from **2a**-H_2 and $CrCl_2$ as a dark-green solid. IR (cm^{-1}): 3177, 2958, 2868, 1622, 1533, 1475, 1443, 1414,1362, 1313, 1258, 1202, 1169, 1026, 833, 746, 548. HRMS-FAB$^+$ (m/z) calcd for $C_{33}H_{50}N_2O_2Cr$ $[M-Cl]^+$ 558.3277; found 558.3270. Anal. Calcd for $C_{33}H_{52}ClN_2O_3Cr$ [(salalen-**2a**)CrCl(H_2O)] (%): C, 64.74; H, 8.56; N, 4.58. Found: C, 64.23; H, 8.66; N, 4.56.

(salalen-2b)CrCl. The title complex was obtained from **2b**-H_2 and $CrCl_2$ as a dark-green solid. IR (cm^{-1}): 3385, 2951, 2864, 1618, 1533, 1477, 1439, 1412, 1391, 1362, 1304, 1254, 1202, 1171, 872, 837, 542. HRMS-FAB$^+$ (m/z) calcd for $C_{37}H_{56}N_2O_2Cr$ $[M-Cl]^+$ 612.3747; found 612.3766. Anal. Calcd for $C_{37}H_{58}ClN_2O_3Cr$ [(salalen-**2b**)CrCl(H_2O)] (%): C, 66.69; H, 8.77; N, 4.20. Found: C, 66.34; H, 8.98; N, 4.26.

(salalen-2c)CrCl. The title complex was obtained from **2c**-H_2 and $CrCl_2$ as a brown solid. IR (cm^{-1}): 3354, 2955, 2868, 1612, 1583, 1528, 1475, 1420, 1391, 1360, 1256, 1200, 1169, 1132, 1105, 872, 835, 758, 542. HRMS-FAB$^+$ (m/z) calcd for $C_{37}H_{50}N_2O_2Cr$ $[M-Cl]^+$ 606.3277; found 606.3296. Anal. Calcd for $C_{37}H_{50}ClN_2O_2Cr$ [(salalen-**2c**)CrCl] (%): C, 69.19; H, 7.85; N, 4.36. Found: C, 69.41; H, 8.49; N, 4.16.

(salalen-2d)CrCl. The title complex was obtained from **2d**-H_2 and $CrCl_2$ as a red-brown solid. IR (cm^{-1}): 3379, 2955, 2868, 1599, 1578, 1526, 1474, 1418, 1360, 1256, 1200, 1169, 1130, 953, 914, 874, 835, 785, 748, 687, 548. HRMS-FAB$^+$ (m/z) calcd for $C_{37}H_{48}Cl_2N_2O_2Cr$ $[M-Cl]^+$ 674.2498; found 674.2490. Anal. Calcd for $C_{37}H_{48}Cl_3N_2O_2Cr$ [(salalen-**2d**)CrCl] (%): C, 62.49; H, 6.80; N, 3.94. Found: C, 64.88; H, 7.33; N, 4.10.

(salalen-3)CrCl. The title complex was obtained from **3**-H_2 and $CrCl_2$ as a brown solid. IR (cm^{-1}): 2957, 2868, 1624, 1533, 1477, 1414, 1387, 1360, 1256, 1238, 1202, 1169, 1026, 876, 835, 808, 783, 745, 548. HRMS-FAB$^+$ (m/z) calcd for $C_{34}H_{52}N_2O_2Cr$ $[M-Cl]^+$ 572.3434; found 572.3412. Anal. Calcd for $C_{34}H_{54}ClN_2O_3Cr$ [(salalen-**3**)CrCl(H_2O)] (%): C, 65.21; H, 8.69; N, 4.47. Found: C, 66.49; H, 9.12; N, 4.19.

(salalen-4)CrCl. The title complex was obtained from **4**-H_2 and $CrCl_2$ as a dark-green solid. IR (cm^{-1}): 3387, 2957, 2868, 1618, 1533, 1477, 1439, 1414, 1391, 1362, 1308, 1258, 1238, 1202, 1169, 874, 839, 783, 748, 548, 492. HRMS-FAB$^+$ (m/z) calcd for $C_{35}H_{54}N_2O_2Cr$ $[M - Cl]^+$ 586.3590; found 586.3570. Anal. Calcd for $C_{35}H_{56}ClN_2O_3Cr$ [(salalen-**4**)CrCl(H_2O)] (%): C, 65.65; H, 8.82; N, 4.38. Found: C, 62.94; H, 9.25; N, 3.75.

(salalen-5)CrCl. The title complex was obtained from **5**-H_2 and $CrCl_2$ as a dark-brown solid. IR (cm^{-1}): 3373, 2957, 2868, 1616, 1533, 1439, 1414, 1391, 1362, 1319, 1256, 1202, 1171, 876, 841, 750, 694, 548, 507. HRMS-FAB$^+$ (m/z) calcd for $C_{38}H_{52}N_2O_2Cr$ $[M - Cl]^+$ 620.3434; found 620.3452. Anal. Calcd for $C_{38}H_{54}ClN_2O_3Cr$ [(salalen-**5**)CrCl(H_2O)] (%): C, 67.69; H, 8.07; N, 4.15. Found: C, 68.19; H, 8.445; N, 3.82.

Copolymerization of Cyclohexene Oxide with CO_2. A 50 mL autoclave was charged with stirring bar, (salalen)CrCl complex (9.9 μmol), and cocatalyst (9.9 μmol). After drying in vacuo for 1 h, cyclohexene oxide (1.0 mL, 9.9 mmol) was added via syringe under Ar. The autoclave was charged with CO_2 to appropriate pressure, and the resulting mixture was stirred for 3 h at 70 °C. The reaction mixture was cooled to room temperature, and CO_2 pressure was slowly released. Phenanthrene was added as an internal standard, and ^{1}H NMR analysis was performed. The resulting polymerization mixture was dissolved with CH_2Cl_2 and poured into a large amount of MeOH to give a precipitation of the copolymer. The precipitate was collected by decantation and dried in vacuo. The enantiomeric excess was determined according to the literature.[25a]

MALDI-TOF Mass Spectrometry. Samples for analysis were prepared by mixing the copolymer (1.0 wt % in THF), a matrix (1,8-dihydroxy-9(10*H*)-anthracenone; dithranol, 5.0 wt % in THF), and a cationizing agent (sodium trifluoroacetate, 1.0 wt %) in the weight ratio of 1/40/1. Then 1.0 μL portions of the mixture were placed onto the hollows on the gold-coated plate and dried under ambient conditions. MALDI-TOF mass spectrometric measurements were performed in the linear mode by using an accelerating voltage of 25 kV. Mass spectra from 1000 laser shots were accumulated to produce a final spectrum. Substance P (MW = 1348.73), Insulin B chain (MW = 3495.95), and Insulin Bovine (MW = 5733.55) were used as internal standards to calibrate the mass scale.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1**-H_2−**5**-H_2 and MALDI-TOF mass spectrum of the copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Lett*. **1969**, *7*, 287–292.

(2) For recent reviews, see: (a) Nakano, K.; Kosaka, N.; Hiyama, T.; Nozaki, K. *Dalton Trans*. **2003**, 4039–4050. (b) Sugimoto, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem*. **2004**, *42*, 5561–5573. (c) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed*. **2004**, *43*, 6618–6639. (d) Darensbourg, D. J. *Chem. Rev*. **2007**, *107*, 2388–2410. (e) Luinstra, G. A. *Polym. Rev*. **2008**, *48*, 192–219.

(3) (a) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577–7579. (b) 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. (c) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc*. **2000**, *122*, 12487–12496.

(4) (a) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc*. **1998**, *120*, 11018–11019. (b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc*. **2001**, *123*, 8738–8749. (c) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed*. **2002**, *41*, 2599–2602. (d) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc*. **2002**, *124*, 14284–14285. (e) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc*. **2003**, *125*, 11911–11924. (f) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.; Yun, H.; Lee, H.; Park, Y.-W. *J. Am. Chem. Soc*. **2005**, *127*, 3031–3037.

(5) (a) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc*. **2002**, *124*, 6335–6342. (b) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc*. **2003**, *125*, 7586–7591. (c) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun*. **2003**, *24*, 194–196. (d) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem*. **2004**, *43*, 1831–1833. (e) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem*. **2004**, *43*, 6024–6034. (f) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc*. **2005**, *127*, 14026–14038. (g) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem*. **2005**, *44*, 4622–4629. (h) Li, B.; Zhang, R.; Lu, X. B. *Macromolecules* **2007**, *40*, 2303–2307. (i) Hongfa, C.; Tian, J. H.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun*. **2008**, 975–977.

(6) (a) Qin, Z. Q.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed*. **2003**, *42*, 5484–5487. (b) Lu, X. B.; Wang, Y. *Angew. Chem., Int. Ed*. **2004**, *43*, 3574–3577. (c) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc*. **2005**, *127*, 10869–10878. (d) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251–6253. (e) Cohen, C. T.; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem*. **2006**, *44*, 5182–5191. (f) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans*. **2006**, 237–249. (g) Lu, X. B.; Shi, L.; Wang, Y. M.; Zhang, R.; Zhang, Y. J.; Peng, X. J.; Zhang, Z. C.; Li, B. *J. Am. Chem. Soc*. **2006**, *128*, 1664–1674. (h) Shi, L.; Lu, X. B.; Zhang, R.; Peng, X. J.; Zhang, C. Q.; Li, J. F.; Peng, X. M. *Macromolecules* **2006**, *39*, 5679–5685. (i) Noh, E. K.; Na, S. J.; Sujith, S.; Kim, S. W.; Lee, B. Y. *J. Am. Chem. Soc*. **2007**, *129*, 8082–8083. (j) Sujith, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. *Angew. Chem., Int. Ed*. **2008**, *47*, 7306–7309.

(7) Sugimoto, H.; Ohtsuka, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem*. **2005**, *43*, 4172–4186.

(8) For recent reviews, see (a) Katsuki, T. *Synlett* **2003**, 281–297. (b) Katsuki, T. *Chem. Soc. Rev*. **2004**, *33*, 437–444. (c) Larrow, J. F.; Jacobsen, E. N. *Top. Organomet. Chem*. **2004**, *6*, 123–152. (d) Baleizao, C.; Garcia, H. *Chem. Rev*. **2006**, *106*, 3987–4043. (e) Matsumoto, K.; Saito, B.; Katsuki, T. *Chem. Commun*. **2007**, 3619–3627.

(9) Li, B.; Wu, G. P.; Ren, W. M.; Wang, Y. M.; Rao, D. Y.; Lu, X. B. *J. Polym. Sci., Part A: Polym. Chem*. **2008**, *46*, 6102–6113.

(10) After our submission, the highest catalytic activity (TOF = 153 h^{-1}) in the copolymerization of CHO with CO_2 under atmospheric pressure of CO_2 was reported. See : Ren, W. M.; Liu, Z. W.; Wen, Y. Q.; Zhang, R.; Lu, X. B. *J. Am. Chem. Soc*., ASAP.

(11) Berkessel, A.; Brandenburg, M.; Leitterstorf, E.; Frey, J.; Lex, J.; Schafer, M. *Adv. Synth. Catal*. **2007**, *349*, 2385–2391.

(12) Saito, B.; Katsuki, T. *Angew. Chem., Int. Ed*. **2005**, *44*, 4600–4602.

(13) Eno, S.; Egami, H.; Uchida, T.; Katsuki, T. *Chem. Lett*. **2008**, *37*, 632–633.

(14) The copolymerization at lower temperatures (25 and 45 °C) resulted in the production of a trace amount of the copolymer.

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

(16) Ooi, T.; Takeuchi, M.; Kameda, M.; Maruoka, K. *J. Am. Chem. Soc*. **2000**, *122*, 5228–5229.

(17) A mixture of (salalen)CrCr and [PPN]Cl can copolymerize propylene oxide with CO_2 to provide poly(propylene carbonate), while a significant amount of cyclic propylene carbonate was also produced; see the Supporting Information.

(18) The use of (salan)CrCl for CHO/CO_2 copolymerization resulted in no production of the copolymer; see the Supporting Information.

(19) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144–148.

(20) Bertocco, A. Precipitation and Crystallization Techniques. In *Chemical Synthesis Using Supercritical Fluids*; Jessop, G. P., Leitner, W., Eds.; Wiley-VCH: Weinheim, 1999.

(21) (a) Sugimoto, H.; Ohshima, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3549–3555. (b) Xiao, Y. L.; Wang, Z.; Ding, K. L. *Chem.—Eur. J.* **2005**, *11*, 3668–3678. (c) Xiao, Y. L.; Wang, Z.; Ding, K. L. *Macromolecules* **2006**, *39*, 128–137. (d) Sugimoto, H.; Kuroda, K. *Macromolecules* **2008**, *41*, 312–317. (e) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 931–933.
(22) Dudev, T.; Lim, C. *J. Phys. Chem. B* **2004**, *108*, 4546–4557.
(23) Chattopadhyay, S.; Drew, M. G. B.; Ghosh, A. *Eur. J. Inorg, Chem.* **2008**, 1693–1701.
(24) Luinstra, G. A.; Haas, G. R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. *Chem.—Eur. J.* **2005**, *11*, 6298–6314.
(25) (a) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009. (b) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007–2008.
(26) Nakano, K.; Nozaki, K.; Hiyama, T. *Macromolecules* **2001**, *34*, 6325–6332.
(27) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501–5510.
(28) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274–7277.
(29) Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2861–2871.
(30) Appiah, W. O.; DeGreeff, A. D.; Razidlo, G. L.; Spessard, S. J.; Pink, M.; Young, V. G.; Hofmeister, G. E. *Inorg. Chem.* **2002**, *41*, 3656–3667.
(31) Seth, P. P.; Robinson, D. E.; Jefferson, E. A.; Swayze, E. E. *Tetrahedron Lett.* **2002**, *43*, 7303–7306.
(32) Yeori, A.; Gendler, S.; Groysman, S.; Goldberg, I.; Kol, M. *Inorg. Chem. Commun.* **2004**, *7*, 280–282.