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Enhanced Asymmetric Induction for the Copolymerization of CO_2 and Cyclohexene Oxide with Unsymmetric Enantiopure SalenCo(III) Complexes: Synthesis of Crystalline CO_2-Based Polycarbonate

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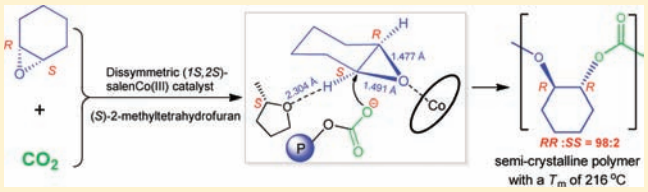
Ⓢ *Supporting Information*

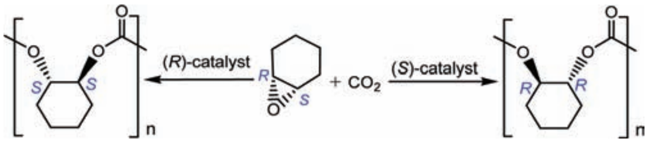
ABSTRACT: Enantiopure metal-complex catalyzed asymmetric alternating copolymerization of CO_2 and *meso*-epoxides is a powerful synthetic strategy for preparing optically active polycarbonates with main-chain chirality. The previous studies regarding chiral zinc catalysts provided amorphous polycarbonates with moderate enantioselectivity, and thus, developing highly stereoregular catalysts for this enantioselective polymerization is highly desirable. Herein, we report the synthesis of highly isotactic poly(cyclohexene carbonate)s from *meso*-cyclohexene oxide using dissymmetrical enantiopure salenCo(III) complexes in conjunction with bis(triphenylphosphine)-iminium chloride (PPNCl) as catalyst. The presence of a chiral induction agent such as (*S*)-propylene oxide or (*S*)-2-methyltetrahydrofuran significantly improved the enantioselectivity regarding (*S*,*S*)-salenCo(III) catalyst systems. Up to 98:2 of *RR*:*SS* was observed in the resultant polycarbonates obtained from the catalyst system based on (*S*,*S*)-salenCo(III) complex **4d** bearing an adamantyl group on the phenolate ortho position, in the presence of (*S*)-2-methyltetrahydrofuran. Primary ONIOM (DFT:UFF) calculations, which were performed to investigate the effect of the competitive coordination of (*S*)-induction agent versus cyclohexene oxide to Co(III) center on enantioselectivity, suggest that the (*S*)-C−O bond in cyclohexene oxide is more favorable for cleavage, due to the interaction between oxygen atom of (*S*)-induction agent and (*S*)-C−H of the coordinated cyclohexene oxide. The highly isotactic poly(cyclohexene carbonate) is a typical semicrystalline polymer, possessing a melting point of 216 °C and a decomposition temperature of 310 °C.



■ INTRODUCTION

The desymmetrization of *meso*-molecules with chiral catalysts or reagents is regarded as a valuable strategy for the synthesis of enantiomerically enriched products.[1] Much attention was paid to the desymmetrization of *meso*-epoxides via nucleophilic ring-opening for establishing two contiguous stereogenic centers.[2] Some highly enantioselective catalyst systems have been developed for the delivery of azide,[3] amine,[4] cyanide,[5] alcohol,[6] thiol,[7] carboxylic[8] and halogen[9] nucleophiles to epoxides, yielding 1,2-difunctionalized fine chemicals in enantiomerically enriched form. When such a powerful synthetic strategy is applied to the alternating copolymerization of CO_2 with *meso*-epoxides, optically active polycarbonates with main-chain chirality can be produced from optically inactive *meso*-monomers. Because the ring-opening of a *meso*-epoxide proceeds with inversion at one of the two chiral centers, a successful asymmetric ring-opening by a chiral catalyst will give optically active polycarbonates with an (*R*,*R*)- or (*S*,*S*)-*trans*-1,2-diol unit. On the basis of this idea, Nozaki et al. reported the first example of the asymmetric copolymerization of CO_2 and cyclohexene oxide (CHO) using an equimolar mixture of $ZnEt_2$ and (*S*)-α,α-diphenyl(pyrrolidin-2-yl)methanol as catalyst (Scheme 1), affording the corresponding polycarbonates with moderate enantioselectivity.[10] Further mechanistic studies demonstrated that a dimeric zinc complex **1** might be the active species and the copolymerization was initiated by CO_2 insertion into the Zn−OEt bond of the complex.[11] Soon after, Coates and co-workers reported the use of hybrid imine-oxazoline zinc-based catalysts **2** for this reaction, which showed similar enantioselectivity but higher activity and controlled molecular weight.[12] On the basis of the mechanistic understanding that dimeric zinc complex was involved in the transition state of the epoxide ring-opening event during CO_2/CHO copolymerization,[11,13] Ding et al. investigated Trost's dinuclear zinc complex **3** for catalyzing this coupling reaction.[14] Unfortunately, after hydrolysis of the resulting polycarbonate with aqueous NaOH, the enantiomeric excess (ee) of the resulting cyclohexane-1,2-diol was determined by chiral GC to be only 18% with an *S*,*S* configuration.

Scheme 1. Asymmetric Alternating Copolymerization of *meso*-Cyclohexene Oxide with CO_2



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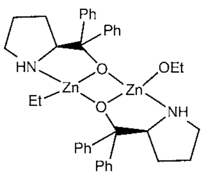

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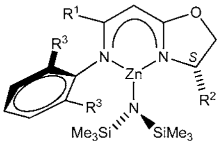

R^1 = Me, CF$_3$, ^{i}Pr
R^2 = (*R*)-Ph, (*S*)-^{i}Pr, (*S*)-^{t}Bu
R^3 = Et, ^{i}Pr

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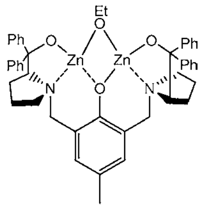

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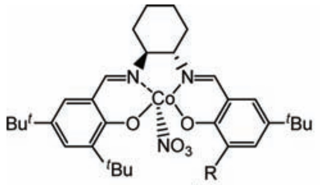
Stimulated by the success with chiral salenCo(III)-catalyzed asymmetric alternating copolymerization of *racemic* terminal epoxides and CO_2,[15] we also applied these systems to the asymmetric copolymerization of CHO and CO_2 under mild conditions.[16] With binary catalyst system of enantiopure complex (1*R*,2*R*)-**4a** (trichloroacetate as the axial anion) and equimolar bis(triphenylphosphine)iminium chloride (PPNCl), copolymerization reaction at ambient temperature and 1.5 MPa CO_2 pressure provided isotactic-enriched poly(cyclohexene carbonate)s with a relatively low enantioselectivity of 38% ee for (*S*,*S*)-configuration.

We noted with great interest a significant difference in enantioselectivity of the polycarbonates obtained from Trost's dinuclear zinc complex **3** and the dimeric zinc complex **1** of (*S*)-*α*,*α*-diphenyl(pyrrolidin-2-yl)methanol, in which the two catalyst systems have the structural similarity, but only slight difference in their symmetry. Similar situation also occurred at imine–oxazoline zinc-based catalysts reported by Coates group, wherein only the hybrid imine–oxazoline zinc complexes showed high activity and good enantioselectivity for this reaction.[12] Obviously, the dissymmetry of the ligand structure plays a significant role in asymmetric induction for enantioselective ring-opening of CHO. These observations lead us to ask the following question: does the dissymmetric environment enhance the asymmetric induction during *meso*-epoxides/CO_2 copolymerization regarding the chiral salenCo(III) catalyst systems? To provide an answer to the question, herein we design a series of unsymmetric enantiopure salenCo(III)NO_3 complexes **4** for the asymmetric copolymerization of CHO and CO_2. Another purpose of this study is to synthesize highly isotactic poly(cyclohexene carbonate) and explore its crystallizability.



(*1S,2S*)-**4a**: R= ^{t}Bu
(*1S,2S*)-**4b**: R= CMe$_2$Ph
(*1S,2S*)-**4c**: R= SiMe$_2$^{t}Bu
(*1S,2S*)-**4d**: R= adamyl

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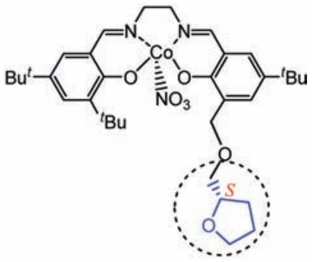

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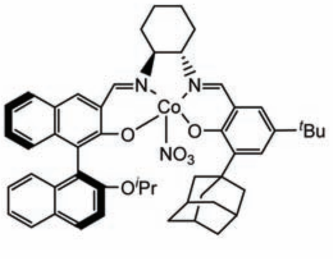

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RESULTS AND DISCUSSTION

The unsymmetrical chiral salen ligands in the complexes **4b–d** were synthesized by the reaction of the corresponding substituted salicyaldehydes on the phenolate ortho positions with the condensation product of Fmoc protected (*S*,*S*)-diaminocyclohexane trifluoroacetate and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (for detailed synthesis procedure, see Supporting Information). Similar procedures were applied to the preparation of complexes **5** and **6**.[17] Since these cobalt complexes are easily dissolved in the neat epoxide surveyed, the catalyzed coupling of CO_2 and CHO does not require any organic cosolvent. Only in some cases for complete conversion of the epoxide, the addition of an organic solvent such as toluene is necessary for effective diffusion of the reactants.

The screening experimental results regarding the use of enantiopure cobalt–salen complexes **4–6** in conjunction with PPNCl as catalysts for the CO_2/CHO copolymerization are summarized in Table 1. We were gratified to discover that the catalyst systems concerning unsymmetric Co(III)–salen complexes exhibited obviously higher enantioselectivity than that regarding symmetric salenCo(III) complex **4a** under the same conditions. Interestingly, the dissymmetry of chiral salen ligands has a negligible effect on catalyst activity. The screening also revealed that complex (1*S*,2*S*)-**4d** bearing one bulky adamantyl and one *tert*-butyl on the phenolate ortho positions was a more effective enantioselective catalyst, producing a quantitative yield of polymer with an *RR*:*SS* ratio of 80:20 in the presence of an organic solvent of toluene at 25 °C (Table 1, entry 5). We speculate that the dissymmetry by the introduction of a bulky group on one phenolate ortho position might distort the geometric configuration of the chiral ligand,[18] which is beneficial for enantioselective ring-opening of CHO.

Owing to the high enantioselectivity of complex (1*S*,2*S*)-**4d**, we selected it as model catalyst to probe the effects of reaction temperature and other factors on enantioselectivity of the resulting polycarbonates. Entries 4–7 show the strong influence of reaction temperature on the enantioselectivity during the copolymerization of CHO and CO_2. When the reaction temperature decreased from 25 to −25 °C, the *RR*:*SS* ratio in the resulting polycarbonates increased from 80:20 to 92:8. Although the lower temperature causes a significant decrease in reaction rate, no cyclic carbonate byproduct was found and the resultant polymers have more than 99% carbonate linkages.

It is generally known that a stereoselective coordination polymerization probably concerns two stereochemistry control mechanisms, including ligand enantiomorphic site and polymer chain-end controls.[19] Similar to the stereoselective transformations of small molecules, coordination polymerization also concerns substrates activation and stereochemistry control of key bond-forming steps, which correlate with the ligand structure of a catalyst. However, unlike the catalytic synthesis of small molecules, in the coordination polymerizations, a polymer chain perhaps remains bound to the active metal center during monomer enchainment. Thus, the stereogenic center from the last enchained monomer unit will have an influence on the stereochemistry of fresh monomer addition.

In previous papers, we have confirmed the existence of polymer chain-end control mechanism during the asymmetric copolymerization of CO_2 and CHO with a binary catalyst system of (1*S*,2*S*)-salenCr(III)X and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), in which an enhanced poly(cyclohexene carbonate) enantioselectivity was observed in

Table 1. Asymmetric Copolymerization of CO_2 and CHO Catalyzed by Chiral SalenCo(III)NO_3 Complexes in Conjunction with PPNCl[a]

entry	catalyst	epoxide	[epoxide]/[cat.]	temp [°C]	time [h]	conv[b] [%]	M_n[c] [g/mol]	PDI[c] [M_w/M_n]	*RR*:*SS*[d]
1	(1*S*,2*S*)-**4a**	CHO	1000	25	4	45	21400	1.13	69:31
2	(1*S*,2*S*)-**4b**	CHO	1000	25	4	46	27500	1.09	72:28
3	(1*S*,2*S*)-**4c**	CHO	1000	25	4	45	23900	1.12	76:24
4	(1*S*,2*S*)-**4d**	CHO	1000	25	4	45	29300	1.10	80:20
5[e]	(1*S*,2*S*)-**4d**	CHO	500	25	24	100	31600	1.17	80:20
6	(1*S*,2*S*)-**4d**	CHO	500	−10	36	60	18300	1.08	87:13
7	(1*S*,2*S*)-**4d**	CHO	400	−25	48	51	11400	1.16	92:8
8[f]	(1*S*,2*S*)-**4d**	CHO/(*R*)-PO	400	−25	48	54	12800	1.14	92:8
9[g]	(1*S*,2*S*)-**4d**	CHO/(*S*)-PO	400	−25	48	46	9600	1.07	97:3
10	(*S*)-**5**	CHO	1000	25	6	44	29300	1.12	56:44
11[h]	(1*S*,2*S*)-**4d**	CHO	300	−25	48	49	10300	1.06	94:6
12[i]	(1*S*,2*S*)-**4d**	CHO	300	−25	48	45	9200	1.14	98:2
13	(*S*,*S*,*S*)-**6**	CHO	500	25	4	40	12900	1.08	92:8
14	(*S*,*S*,*S*)-**6**	CHO	500	0	36	32	9900	1.12	95:5

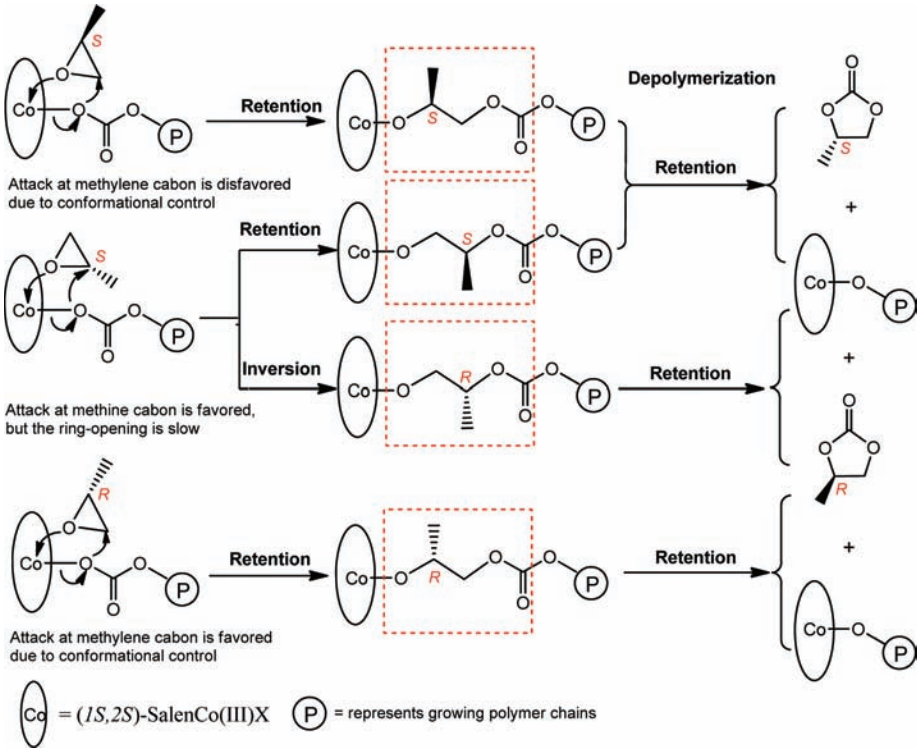
[a] The reaction was performed in neat CHO in 40 mL autoclave, Co(III) complex/PPNCl = 1/1 (molar ratio); 1.5 MPa CO_2 pressure for entries 1−5, 10, and 13; 0.8 MPa CO_2 pressure for entries 6−9, 11, 12, and 14; the resulting polycarbonates have >99% carbonate linkages as determined by ^{1}H NMR spectroscopy. [b] The conversion was determined by ^{1}H NMR spectroscopy. [c] Determined by GPC against polystyrene standards in tetrahydrofuran. [d] Measured by hydrolyzing the polymer and analyzing the resulting diol by chiral GC. [e] The reaction was carried out in toluene solution [CHO]/[toluene] = 1:1 (volume ratio). [f] CHO/(*R*)-PO = 1/3 (molar ratio), the resultant polycarbonates include 16.7% cyclohexene carbonate linkages (molar ratio), determined by ^{1}H NMR spectroscopy; after the depolymerization of the resulting polycarbonates by ^{t}BuOLi, the ee of the resulting propylene carbonate is 97%, determined by chiral GC. [g] CHO/(*S*)-PO = 1/3 (molar ratio), the resulting polycarbonates include 37.5% cyclohexene carbonate linkages, and the ee of the propylene carbonate resulting from polycarbonate degradation is 70%. [h] In the presence of (*S*)-2-methyltetrahydrofuran, CHO/(*S*)-2-methyltetrahydrofuran = 1/1 (molar ratio). [i] In the presence of (*S*)-2-methyltetrahydrofuran, CHO/(*S*)-2-methyltetrahydrofuran = 1/3 (molar ratio).

the presence of (*R*)-propylene oxide {(*R*)-PO}.[20] In the present study, we also performed some control experiments to investigate the effect of chiral PO on the enantioselective ring-opening of CHO. A mixture of epoxides of CHO and (*R*)-PO (1:3, moral ratio) was used for polymerization with CO_2 catalyzing by complex (1*S*,2*S*)-**4d** in conjunction with PPNCl, but the ee of cyclohexane-1,2-diol from the hydrolysis of the resultant polycarbonate with aqueous NaOH did not show any change in comparison with in the absence of (*R*)-PO. This rather surprising result indicates that the stereochemistry in the CO_2/CHO copolymerization concerning chiral cobalt−salen catalyst systems does not correlate with polymer chain-end control mechanism. By contrast, substituted (*S*)-PO for (*R*)-PO led to a significant increase in enantioselective ring-opening of CHO, and the formed polycarbonate with an *RR*:*SS* ratio of 97:3. The polymer resulted from the CHO/(*R*)-PO/CO_2 terpolymerization (CHO/PO = 1/3, molar ratio) contains less than 17% cyclohexene carbonate units after 54% conversion, and the stereochemistry at the methine carbon of (*R*)-PO up to 98.5% incorporated into polycarbonate remains during the polymerization. On the contrary, the polycarbonate obtained from the CHO/(*S*)-PO/CO_2 terpolymerization (CHO/PO = 1/3, molar ratio) contains about 38% cyclohexene carbonate units after a conversion of 46%, and (*S*)-PO of 15% has a change in stereochemistry at the methine carbon with inversion. When CHO and (*S*)-PO in the mixture epoxides are equimolar, the resulting terpolymer contains about 69% cyclohexene carbonate units after a conversion of 21%. ^{1}H NMR analysis of the samples from the CHO/(*S*)-PO/CO_2 terpolymerization at various time points demonstrates that with binary (1*S*,2*S*)-**4d**/PPNCl catalyst system (*S*)-PO shows less reactivity than CHO, because the asymmetric induction of the chiral cobalt complex results in ring-opening of a certain amount of (*S*)-PO incorporated into the terpolymer occurring at the methine carbon (Scheme 2). Therefore, we tentatively assume that the competition coordination of (*S*)-PO to the central metal ion makes a contribution to chiral induction for enantioselective ring-opening of CHO (Scheme 3). One can imagine that a stereodynamic (*S*)-PO ligand populates a distinctive chiral conformation upon coordination to the metal ion of a chiral catalyst such as (1*S*,2*S*)-**4d**. The chirality of the metal complex is then amplified and this may increase asymmetric induction in the coordination of CHO and its further enantioselective ring-opening during the polymerization with CO_2. In previous studies, we have confirmed that the propagating carboxylate species easily dissociate from the central cobalt ion by electrospray ionization mass spectrometry, in combination with some control experiments.[21] The dissociated polymer chain anion further selectively attacks at the (*S*)-configuration carbon atom of a bound CHO induced by (*S*)-PO surrounding the Co(III) ion via competition coordination (Scheme 3).

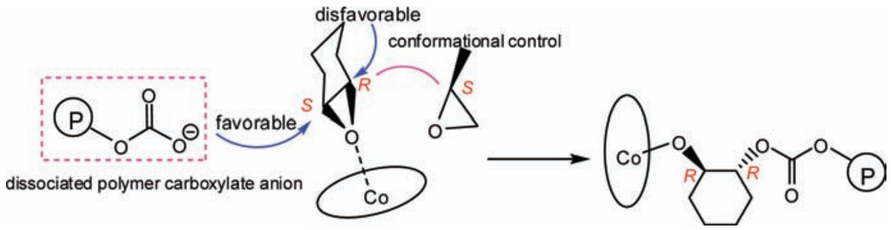
To test the hypothesis outlined in Scheme 3, we evaluated a cobalt−salen complex **5** for the CO_2/CHO copolymerization. The complex **5** has nonchiral diamine backbone but bears an *S*-configurational coordination group on the phenolate ortho position in order to simulate the role of (*S*)-PO in the CHO/(*S*)-PO/CO_2 terpolymerization. The resulting polymers also exhibit certain enantioselectivity, and after hydrolysis with aqueous NaOH, the ee of the obtained cyclohexane-1,2-diol was determined to be 12% with an *R*,*R*-configuration. This result indicates that the chiral group on the phenolate ortho position also plays an important role for stereoselective ring-opening of CHO during the copolymerization with CO_2.

In consideration for the reactivity of (*S*)-PO, we chose (*S*)-2-methyltetrahydrofuran (a nonreactive reagent but having a comparable coordination ability of epoxide) as chiral induction agent for investigating its effect on asymmetric ring-opening of CHO during the copolymerization with CO_2. A similar increase in chiral induction in the ring-opening of CHO was observed in

Scheme 2. The Preferential Stereochemistry Involved in the Ring-Opening of (*S*)-PO or (*R*)-PO in the Central Cobalt Ion of (1*S*,2*S*)-4 Complexes during the Polymerization with CO_2



Scheme 3. The Preferential Stereochemistry Involved in the Ring-Opening of CHO in the Central Cobalt Ion of (1*S*,2*S*)-4 Complexes in the Presence of (*S*)-PO during the Polymerization with CO_2



the system concerning the substitution of (*S*)-2-methyltetrahydrofuran for (*S*)-PO (Table 1, entries 11 and 12). The competitive coordination of (*S*)-2-methyltetrahydrofuran and CHO to Co(III) center resulted in a significant decrease in copolymerization rate. The ^{13}C NMR spectra of the resultant copolymers in carbonyl region also confirmed an obvious increase in tacticity[22] due to the chiral induction of (*S*)-2-methyltetrahydrofuran (Figure 1A).

To obtain further information about the competitive coordination of CHO and (*S*)-PO to Co(III) center, primary ONIOM (DFT:UFF) calculations have been performed. The results show that the coordination energy of CHO is larger than that of (*S*)-PO by 3.75 kcal/mol, suggesting a priority of CHO over (*S*)-PO in the coordination to metal center. An attempt to computationally locate a geometrical structure in which both CHO and (*S*)-PO coordinate to the metal center was fruitless mainly due to steric effects. However, a CHO-coordinated structure with a weak interaction between CHO and (*S*)-PO was located instead (Scheme 4). The prior coordination of CHO but not (*S*)-PO to Co(III) is in line with the larger coordination energy of CHO. It was unexpectedly found that the interaction caused an enhanced difference (0.014 Å) between (*S*)-C−O (1.491 Å) and (*R*)-C−O (1.477 Å) bond lengths of the coordinated CHO (Scheme 4) compared to that (1.496 − 1.490 = 0.006 Å) in the absence of (*S*)-PO (see Figure S1b in Supporting Information). This suggests that the (*S*)-C−O bond is more favorable to cleavage. Such result may account for the experimental observation that the presence of (*S*)-PO increased the stereoselectivity of CHO ring-opening. Similarly, with (*S*)-2-methyltetrahydrofuran as chiral induction agent, a weak interaction was also found between the coordinated CHO and (*S*)-2-methyltetrahydrofuran (Scheme 4B). As expected, the same difference (0.014 Å) between (*S*)-C−O (1.491 Å) and (*R*)-C−O (1.477 Å) bond lengths of the coordinated CHO was detected. The coordination energy of (*S*)-2-methyltetrahydrofuran was computed to be 19.23 kcal/mol, which is smaller than that (32.53 kcal/mol) of CHO by 13.3 kcal/mol, suggesting a favorable coordination of CHO over (*S*)-2-methyltetrahydrofuran.

Furthermore, we prepared a novel multichiral (*S*,*S*,*S*)-Co(III) complex **6** with a sterically hindered coordination environment around the central metal ion. Both (1*S*,2*S*)-1,2-diaminocyclohexane backbone and the *S*-configured 2′-isopropyloxy-1,1′-binaphthyl of the ligand cooperatively provide chiral environment

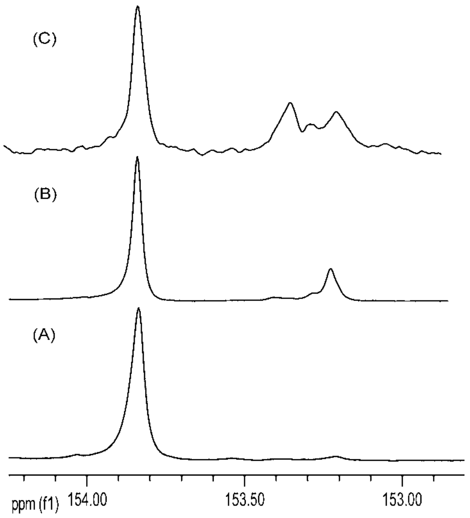
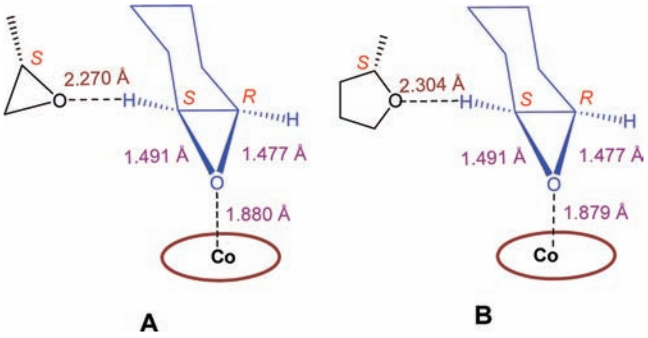


Figure 1. Carbonyl region of ^{13}C NMR spectra of the polycarbonates resulted from the copolymerization of CO_2 and CHO catalyzed by (A) (1*S*,2*S*)-**4d** in the presence of (*S*)-2-methyltetrahydrofuran, *RR*:*SS* = 98:2; (B) (1*S*,2*S*)-**4d**, *RR*:*SS* = 92:8; (C) *racemic* **4a**, *RR*:*SS* = 50:50.

Scheme 4. Schematic Representation of the Optimized CHO-Coordinated Structure with an Interaction between CHO and (*S*)-Induction Agent {A, (*S*)-PO; B, (*S*)-2-Methyltetrahydrofuran[a]



[a] See Figures S1 and S2 in Supporting Information for their 3D structure. The O···H distance of 2.270 or 2.304 Å suggests an interaction between CHO and (*S*)-PO or (*S*)-2-methyltetrahydrofuran (the sum of van der Waals radius of O and H atoms is 2.72 Å).

around the central metal ion. With (*S*,*S*,*S*)-Co(III) complex **6** and PPNCl as catalyst, an enhanced enantioselectivity was observed in the resultant poly(cyclohexene carbonate)s at both 25 and 0 °C (Table 1, entries 13 and 14). Unfortunately, further decrease in reaction temperature caused a substantial loss in catalytic activity, and thus difficultly obtaining copolymers even after a prolonged time. Additionally, the addition of (*S*)-2-methyltetrahydrofuran did not result in an obvious increase in enantioselctivity, but cause a great loss in reaction rate.

Selective transformation of CO_2 into degradable polycarbonates by the alternating copolymerization with epoxides represents one green polymerization process for potential large-scale utilization of CO_2, an abundant, inexpensive, and nontoxic renewable carbon resource.[23] Unfortunately, all of the previously reported CO_2-based polycarbonates are amorphous, and their corresponding low thermal deformation resistance makes them difficult to use as structural materials. For any given polymer, the crystallization behavior of a polymer is determined mainly by the relative stereochemistry (the spatial arrangement of atoms or groups in a polymeric unit) of adjacent locations in the polymeric chains.[24] Herein, we explore the crystallizability of the highly isotactic poly(cyclohexene carbonate)s by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) methods.

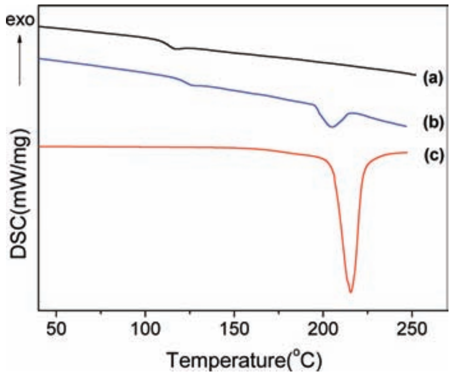


Figure 2. DSC thermograms of various poly(cyclohexene carbonate)s. (a) Atactic PCHC, (b) (*R*)-PCHC-92, and (c) (*R*)-PCHC-98. The samples were crystallized isothermally at 180 °C for 60 min.

Initially, the crystallization and melting behavior of the PCHCs were studied by means of DSC in a flowing-nitrogen atmosphere. Figure 2 shows the DSC thermograms of PCHCs with various degrees of isotacticity in the second heating cycle. Only a single glass transition peak was observed at around 115 °C for the atactic PCHC, demonstrating that this polymer is completely amorphous (Figure 2a). The isotacticity of PCHC has the critical influence on its crystallinity. It was found that the samples with less than 90% isotacticity did not show any crystallization. We were delighted to find that the (*R*)-PCHC-92 (*RR*:*SS* ratio in the resultant polycarbonate is 92:8) gave a T_g of 122 °C and a very small melting endothermic peak at 207 °C with the melting enthalpy of (ΔH_m) 3.92 J/g, indicating a very low degree of crystallinity (Figure 2b). Regarding the highly isotactic polymer (*R*)-PCHC-98 (*RR*:*SS* ratio in the polycarbonate is 98:2), one should first notice from the DSC trace that the T_g peak has disappeared, while a quite sharp and high crystallization endothermic peak is now found at 216 °C with ΔH_m = 22.50 J/g (Figure 2c). The result implies that the crystallization ability of PCHC is greatly enhanced with the increase in isotacticity.

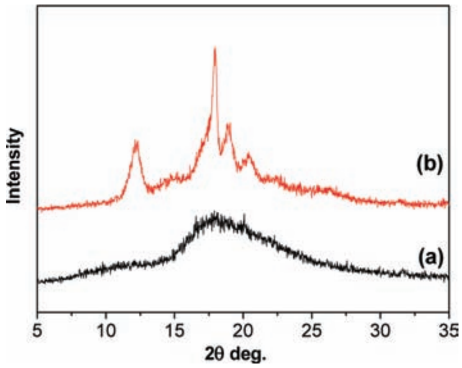


Figure 3. WAXD profiles of (a) atactic PCHC and (b) (*R*)-PCHC-98.

Figure 3 shows the WAXD profiles of atactic PCHC and (*R*)-PCHC-98, which were crystallized isothermally at 180 °C for 60 min and measured at room temperature in air atmosphere.[25] No diffraction was observed for the atactic PCHC, confirming its amorphous feature (Figure 3a). On the contrary, for (*R*)-PCHC-98 sample, sharp diffraction peaks were observed at 2θ values of 12.2, 17.9, 19.0, and 20.4°, demonstrating that the isotactic PCHC is a typical semicrystalline polymer (Figure 3b).

■ CONCLUSIONS AND OUTLOOK

In summary, we have demonstrated that the dissymmetry of the ligand concerning enantiopure salenCo(III) complexes as catalysts is beneficial for enantioselective ring-opening of *meso*-cyclohexene oxide during the asymmetric copolymerization with CO_2. With binary (1*S*,2*S*)-**4d**/PPNCl catalyst system, a significant increase in enantioselective ring-opening of CHO was observed in the presence of (*S*)-PO or (*S*)-2-methyltetrahydrofuran, and the *RR*:*SS* ratio of the resultant polycarbonate was up to 98:2, the highest record in this asymmetric polymerization catalysis. Also, we confirmed that the stereochemistry in the CO_2/CHO copolymerization concerning chiral cobalt−salen catalyst systems did not correlate with polymer chain-end control mechanism. In addition, the isotactic poly(cyclohexene carbonate) (PCHC) is a typical semicrystalline thermoplastic, and possesses a high T_m of 216 °C. Further studies on detailed crystallization behavior and kinetics are currently underway in our laboratory.

The discovery of the first semicrystalline CO_2-based polycarbonate,[26] highly isotactic poly(cyclohexene carbonate), is a good start to develop a more environmentally benign route for producing polycarbonates with excellent properties, though production on a large scale has proven difficult nowadays, due to relatively low catalyst efficiency and related process limitations of low polymerization temperatures. Further efforts will focus on designing highly stereoregular catalysts at enhanced temperatures, and developing new CO_2-based crystalline polymers with improved thermal and mechanical properties comparable to that of polyolefins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental procedures for the synthesis of various unsymmetric enantiopure ligands and their cobalt(III) complexes, as well as their characterizations. X-ray crystallographic file in CIF format for the structure determination of one dissymmetric salenAl(III) complex bearing one bulky adamantyl and one *tert*-butyl at the phenolate ortho positions. Synthetic procedures of various poly(cyclohexene carbonate)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(18) Although much effort was placed in attempts to clarify the structure of these dissymmetric salenCo(III) complexes, we failed to isolate their crystals. Fortunately, we succeeded in obtaining the X-ray crystal structure (Figure S23 in Supporting Information) of one dissymmetric salenAl(III) complex bearing one bulky adamantyl and one *tert*-butyl at the phenolate ortho positions. The two N−Al−O angles are 160° and 96°, indicating a distorted configuration. This is very different from the symmetric SalenAl(III) complexes bearing ethylene diamine backbone or/and cyclohexane diamine backbone {See: (a) Darensbourg, D. J.; Billodeaux, D. R. *Inorg. Chem.* **2005**, *44*, 1433−1742. (b) Rutherford, D.; Atwood, D. A. *Organometallics* **1996**, *15*, 4417−4422 }.

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(25) The complete alternating polycarbonate shows highly thermal stability and possesses a decomposition temperature of 310 °C. Additionally, no degradation to the corresponding cyclic carbonate occurred even at 180 °C for 24 h under a nitrogen atmosphere.

(26) It is worthwhile noting here parenthetically that Coates and co-workers have previously mentioned the existence of a T_m of 220 °C in their synthesized PCHC with 86% isotacticity, though they did not afford the DSC thermgram of the sample. See: reference 12.