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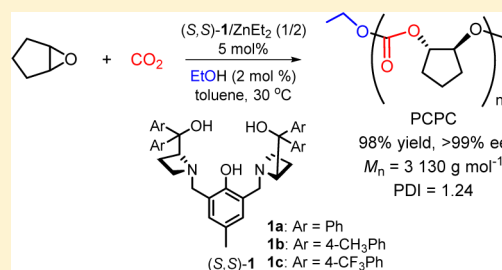
Asymmetric Copolymerization of Cyclopentene Oxide and CO₂ Using a Dinuclear Zinc–AzePhenol Catalyst: Enlightened by DFT Calculations

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S Supporting Information

ABSTRACT: Optically active polycarbonates (PCs) are considered as candidates for new and valuable materials because of their well-defined chemical structures and special physical properties. Previous studies on asymmetric alternating copolymerization of cyclopentene oxide (CPO) and CO₂ regarding chiral zinc catalysts provided poly(cyclopentene carbonate) (PCPC) with moderate enantioselectivity, and thus, the development of highly efficient catalysts for this enantioselective polymerization is highly desirable. This research work is enlightened by the DFT calculations. In this paper, we clearly describe the use of intramolecular dinuclear zinc–AzePhenol complex as a high performance catalyst for the asymmetric copolymerization of CPO and CO₂, affording completely alternating PCPC under very mild conditions (1 atm CO₂, 30 °C) in 98% yield with >99% enantioselectivity for (S,S)-configuration. The dinuclear catalyst is prepared in situ from the reaction of multitdentate semiazecrown ether ligand and ZnEt₂, followed by treatment with an alcohol additive. In addition, our previous studies indicated that this catalyst also showed excellent enantioselectivity in the asymmetric copolymerization of cyclohexene oxide (CHO) and CO₂. In order to obtain more information on the mechanism of the catalytic copolymerization, the chemical structures of PCPC are characterized by ¹H NMR and ¹³C NMR spectroscopy, and the nonlinear effect is also investigated in this copolymerization. A plausible catalytic cycle for the present reaction system is outlined. The reaction of chiral ligand with ZnEt₂, followed by the ethyl group exchange with EtOH, affords the ethoxy-bridged dinuclear zinc complex. The copolymerization reaction is initiated by the insertion of CO₂ into the Zn–OEt bond to give a carbonate–ester-bridged complex. The two zinc centers are situated sufficiently close to each other to allow a synergistic effect in the copolymerization, meaning that one zinc atom acts as Lewis acid to activate the epoxide, the other is responsible for carbonate propagation through the nucleophilic attack of carbonate ester at the back side of the *cis*-epoxide by a six-membered transition state. Furthermore, the dinuclear zinc structure of the catalyst remains intact throughout the catalytic copolymerization. The proposed mechanism implies that the intramolecular dinuclear zinc catalyst is very important for future research into the copolymerization of other epoxides with CO₂.



INTRODUCTION

Polycarbonates (PCs) have gained major industrial and academic interest owing to the diversity in their properties, affording both commodity plastics and engineering plastics.¹ The copolymerization of epoxides with CO₂, as one of the methods to utilize CO₂,² has been applied to essential synthetic process for the preparation of PCs.³ Since it was first reported in the year of 1969,⁴ the copolymerization reaction of epoxides and CO₂ has been studied extensively, and great progress has been made.⁵

Chiral PCs are considered as candidates for new and valuable materials because of its well-defined chemical structures, special physical properties and stereoselective degradability. Recently, the catalytic asymmetric copolymerization of epoxides with CO₂, generating optically active PCs, has been an appealing and demanding area of research.⁶ In 1999, the first catalytic asymmetric example of this methodology by using cyclohexene oxide (CHO) with CO₂ was reported by Nozaki and co-workers.^{7a} Since then, several groups have devoted their efforts

to developing efficient and adapted catalysts for the title reaction.

The copolymerization of CHO with CO₂ afforded poly(cyclohexene carbonate) (PCHC) with moderate enantiomeric excess (ee) of 73% by using an equimolar mixture of ZnEt₂ and (S)- α,α -diphenyl(pyrrolidin-2-yl)methanol as catalyst. In the presence of additional ethanol, the enantioselectivity increased up to 80% ee.⁷ Further mechanistic studies demonstrated that an intermolecular dinuclear zinc complex might be the active species, and the copolymerization was initiated by CO₂ insertion into the Zn–OEt bond of the complex.⁷ Soon after, Coates et al. reported the use of hybrid imineoxazoline zinc-based catalyst in 2000 for this copolymerization with similar enantioselectivity (72% ee).⁸ On the basis of the mechanistic understanding that dimeric zinc complex was involved in the

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transition state of the epoxide ring-opening event during CHO/CO₂ copolymerization, more recently, they also designed an enantioselective zinc β -diiminate catalyst for the synthesis of PCHC with 94% enantioselectivity.⁹ Other examples using zinc were reported, including an intramolecular dinuclear complex developed by Ding et al.,¹⁰ and a series of chiral amido-oxazolinone complex developed by Du and co-workers,¹¹ which yielded chiral PCHC with 18% ee and 42% ee, respectively.

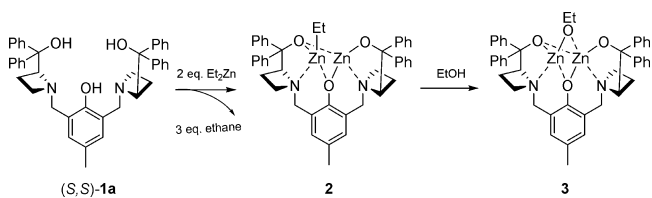
An optically active dinuclear aluminum complex was also used to catalyze the copolymerization of CHO and CO₂ with moderate enantioselectivity (60–82% ee) by Sugimoto et al. in 2012.¹²

Lu and colleagues reported a family of chiral salen cobalt complex for this copolymerization of CHO and CO₂.¹³ A binary catalyst system that consisted of an unsymmetrical chiral salen cobalt complex and bis(triphenylphosphine)iminium chloride (PPNCl) exhibited high enantioselectivity (up to 96% ee) in the copolymerization of CHO and CO₂.^{13d,e} And a dinuclear cobalt complex with a rigid bridging biphenyl linker afforded the copolymer product with 98% enantioselectivity.^{13f}

CHO is an inexpensive, easy-to-handle substrate for highly selective producing of polycarbonate for most catalyst systems under a broad range of reaction conditions. As such, many groups have incorrectly deduced that their catalyst's high selectivity for preparation of PCHC should suit all other potential monomers.^{5p} In fact, although six-membered epoxides (CHO) has been successfully polymerized employing CO₂ with high enantioselectivity under mild operating conditions, the related five-membered epoxides (cyclopentene oxide, CPO) has hardly been well studied on the copolymerization with CO₂,^{5p} probably due to their poor polymeric ability and the tendency to produce the corresponding five-membered ring cyclic carbonate monomer.^{5p,14} A significant decrease in reactivity and enantioselectivity was mentioned in the reported zinc-based catalyst and cobalt-based catalyst in the coupling reaction of CPO with CO₂,^{7,13f} although CPO and CHO differ only by one methylene group. So far, only limited highly enantioselective examples have been reported in the copolymerization of CPO and CO₂.^{9,13f,15} As a consequence, the synthesis of stereoregular PCs from CPO and CO₂ is challenging.

Recently, we reported an intramolecular dinuclear zinc–AzePhenol complex **2** [Zn₂EtL, L = (S,S)-**1a**] prepared by reacting the chiral ligand (S,S)-**1a** with two equivalents of diethylzinc wherein three equivalents of ethane evolved (Scheme 1). There was a dynamic balance between the (Zn₂EtL)_n and Zn₂EtL.¹⁶ The in situ generated complex **2** was efficient to conduct catalytic asymmetric Friedel–Crafts alkylation of unprotected pyrrole with a broad range of chalcones affording the products in excellent yields (up to 99%) and excellent enantioselectivities (up to 99% ee).

Scheme 1. Dinuclear Zinc–AzePhenol Complex



In addition, when complex **2** was used for the asymmetric alternating copolymerization of CHO and CO₂ in the presence of 2 mol % EtOH, highly isotactic PCHC composed of 1,2-cyclohexanediol units was obtained in quantitative yield and high enantioselectivity of up to 93.8% ee.¹⁷ This enantioselectivity was much better than that of Trost's dinuclear zinc–ProPhenol catalyst in the same reaction (only 18% ee),^{10a} although our dinuclear zinc–AzePhenol complex is similar to Trost's in structure. This huge improvement in enantioselectivity may be owing to the relatively rigid ligand skeleton and appropriate chiral microenvironment provided by the four-membered heterocycle. Density functional theory (DFT) calculations of the transition state energies indicated a calculated ee value of approximately 92.2%, which was very close to the experimental outcome (93.8% ee).¹⁷

Encouraged by the above results, theoretical calculations were carried out by using the same model in the copolymerization of CO₂ with CPO instead of CHO. Gratifyingly, a predictive enantioselectivity of 95.3% ee for (S,S)-configuration was obtained. To confirm the theoretical calculation results, herein, we report the use of dinuclear zinc–AzePhenol complex in the asymmetric copolymerization of CPO and CO₂ to afford completely alternating poly-(cyclopentene carbonate) (PCPC) with up to >99% ee. To our knowledge, this study represents the first example of an intramolecular dinuclear zinc catalytic asymmetric copolymerization of not only CHO and CO₂ but also CPO and CO₂ both with excellent enantioselectivity.^{15,17}

RESULTS AND DISCUSSION

Theoretical Calculation. Theoretical calculations were carried out to study the intramolecular S_N2 attack of carbonate ester at the back side of the *cis*-epoxide (CPO) based on the model of the transition state for the CHO/CO₂ copolymerization system,¹⁷ which was the stereoselectivity-determining step and the rate-determining step according to the previous reports.¹⁸ The calculation model was built according a similar catalyst crystal structure information on intramolecular dinuclear zinc–ProPhenol complex.^{10a} We optimized the transition states and calculated the free energies of the S_N2 reaction step in toluene at the ω B97XD/6-31G(d)¹⁹ level by using the conductor-like polarizable continuum model (CPCM) method,²⁰ which was successfully applied by Williams et al.^{18f} on the study of similar reaction mechanisms. Figure 1 illustrates the optimized structures of the two key transition

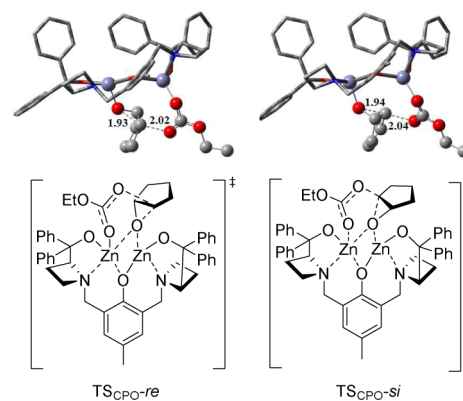


Figure 1. Structures of intramolecular S_N2 transition states optimized at the ω B97XD/6-31G(d) level.

Table 1. Asymmetric Alternating Copolymerization of CPO and CO₂^a

entry	solvent	additive	temp (°C)	yield ^b (%)	<i>M_n</i> ^c (g mol ⁻¹)	PDI ^c	ee ^d (%)
1	toluene	EtOH	50	97	9040	1.25	85
2	toluene	CH ₃ OH	50	89	7620	1.30	70
3	toluene	ⁿ PrOH	50	61	9030	1.19	84
4	toluene	^t PrOH	50	95	9230	1.32	81
5	toluene	ⁿ BuOH	50	88	8590	1.25	77
6	toluene	<i>sec</i> -butyl alcohol	50	84	5250	1.31	84
7	toluene	BnOH	50	60	4230	1.37	83
8	toluene	PhCOOH	50	88	7050	1.32	81
9	toluene	<i>p</i> -NO ₂ PhOH	50	NR ^e	<i>f</i>	<i>f</i>	<i>f</i>
10	toluene	<i>p</i> -cresol	50	>99	7510	1.25	77
11	toluene	EtOH	60	99	10100	1.27	60
12	toluene	EtOH	40	96	4240	1.36	96
13	toluene	EtOH	30	98	3130	1.24	>99
14 ^g	toluene	EtOH	20	<5	<i>f</i>	<i>f</i>	<i>f</i>
15	hexane	EtOH	30	NR ^e	<i>f</i>	<i>f</i>	<i>f</i>
16	DCE	EtOH	30	<10	1800	1.29	<i>f</i>
17 ^h	toluene	EtOH	30	95	5420	1.25	95
18 ⁱ	toluene	EtOH	30	78	6210	1.31	92

^aUnless otherwise noted, all reactions performed by using 5 mol % ligand (S,S)-1a, 10 mol % ZnEt₂, and 2 mol % EtOH, under 1 atm CO₂ pressure for 36 h. ^bIsolated yield. ^cEstimated by gel-permeation chromatography analysis by using a polystyrene standard. ^dHydrolyzing the polymer, derivatizing of the resultant diol using benzoyl chloride, and then determining the ee of the dibenzoate by chiral HPLC. ^eNR: No reaction. ^fNot determined. ^gThe reaction time was 72 h. ^hLigand 1b was used. ⁱLigand 1c was used.

states, that is, TS_{CPO-*re*} (associated with (R,R)-product) and TS_{CPO-*si*} (associated with (S,S)-product). All calculations were carried out with Gaussian 09 programs.²¹

The calculated results showed that TS_{CPO-*si*}, which formed the experimentally observed major (S,S)-product, was favored, by 2.2 kcal mol⁻¹ compared to TS_{CPO-*re*} (Figure 1). This energy value would be in agreement with an ee value of about 95.3% (The predictive ee value is obtained by two formulas, see Supporting Information). This finding suggests that higher enantioselectivity should be achieved in the asymmetric copolymerization of CPO and CO₂ than that of CHO and CO₂ by using complex 2 combined with EtOH additive.

Condition Optimization. Experiments were carried out to confirm the above theoretical calculations. Initially, we conducted the copolymerization of CO₂ and CPO in the presence of 5 mol % of ligand (S,S)-1a, 10 mol % ZnEt₂ and 2 mol % EtOH additive. The copolymerization reaction was carried out at one atm of CO₂ in toluene at 50 °C for 36 h, giving PCPC in 97% yield with a *M_n* value of 9 040 g mol⁻¹ and a relatively narrow polydispersity (PDI = *M_w*/*M_n*) of 1.25. The enantioselectivity of the copolymerization reaction was determined by a similar procedure by previous report.¹⁷ The treatment of PCPC with aqueous NaOH afforded cyclopentane-1,2-diol, followed by the transformation into its dibenzoate. The ee value of dibenzoate was determined by HPLC analysis. To our delight, the enantioselectivity of the resulting dibenzoate was up to 85% ee with (S,S)-configuration (Table 1, entry 1).

Since the ethanol additive has a significant impact on the catalysis of the polymerization according to the previous reports,^{7,10,17} a variety of protonic additives, such as alcohols, phenols, and benzoic acid, were then screened in the

asymmetric copolymerization of CPO and CO₂ (Table 1, entries 2–10). Under the experimental conditions, EtOH was found to be superior to the other additives in terms of enantioselectivity up to 85% ee (Table 1, entries 1 versus 2–10). So EtOH was chosen as the best additive for the asymmetric copolymerization of CPO and CO₂ to assess other reaction parameters.

Temperature proved to have a distinctive effect on the ee value. An increase in temperature from 50 to 60 °C resulted in a decrease in enantioselectivity from 85 to 60% ee (Table 1, entry 11), although the molecular weight increased. Whereas decreasing the reaction temperature from 50 to 40 °C led to an enhancement in enantioselectivity from 85 to 96% ee (Table 1, entry 12). Lowering the temperature to 30 °C resulted in an ee value of up to >99% (Table 1, entry 13). On decreasing the reaction temperature to 20 °C, the copolymerization reaction was almost not initiated (Table 1, entry 14).

The asymmetric copolymerization reaction seriously depended on the solvents. It could be accomplished smoothly in toluene, however, almost no copolymerization reaction occurred in hexane or 1,2-dichloroethane (DCE) (Table 1, entries 15 and 16).

Ligands 1b with a slightly electron-rich group and 1c bearing a strongly electron-withdrawing trifluoromethyl group were also used, respectively. The ligand 1b provided PCPC with a slightly decreased yield of 95% and enantioselectivity of 95% ee (Table 1, entry 17). The ligand 1c provided PCPC in a moderate yield of 78% with 92% ee (Table 1, entry 18).

The chiral PCPC obtained from this highly enantioselective copolymerization reaction of CPO and CO₂ can be easily hydrolyzed to give enantiopure trans-cyclopentane-1,2-diol by

using aqueous NaOH. This is a promising alternative strategy for the synthesis of chiral cyclopentane-1,2-diol.²²

Polymer Characterization. The chemical structures of the PCPC formed with different enantioselectivity are investigated. Although we have not given the accurate assignment of the microstructure of PCPC, significant differences both in the carbonyl and methane regions between the atactic and highly isotactic copolymers are easily identified by ¹³C NMR spectroscopy (Figure 2). The ¹³C NMR spectra of PCPC

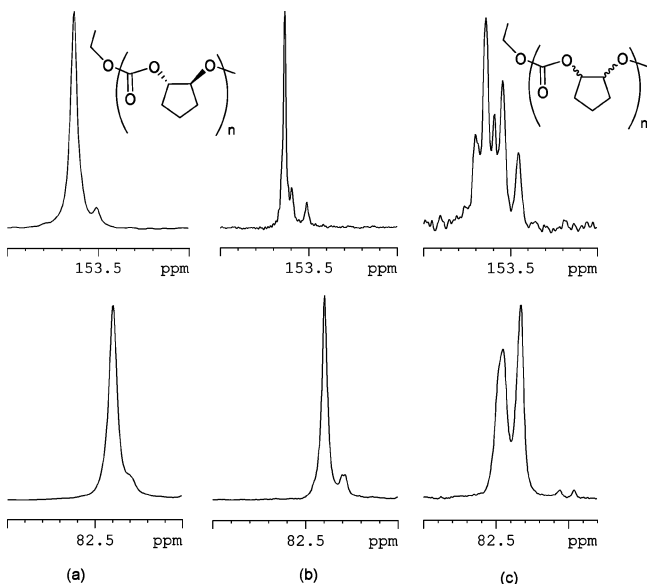


Figure 2. Carbonyl (above) and methane (below) regions of ¹³C NMR spectra of PCPCs. (a) ee >99%; (b) ee = 85%; (c) ee = 0%.

with >99% enantioselectivity is indicative of an highly isotactic copolymer, as previously reported by Lu and co-workers using dinuclear cobalt catalyst.^{13f}

The completely alternating nature (>99% carbonate linkage) of the copolymer was reflected by the ¹H NMR spectroscopic analysis (Figure 3). The signal at 4.22–4.17 ppm, which

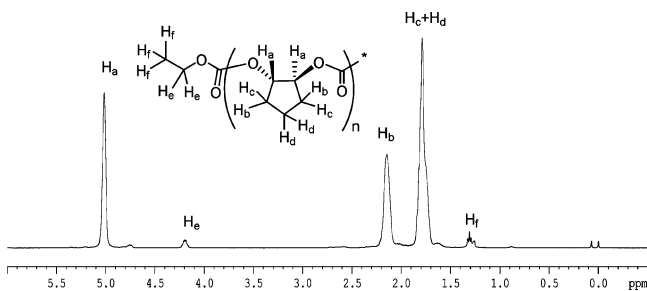


Figure 3. ¹H NMR spectrum of a representative sample of PCPC.

assigned to methylene protons (H_e) of the ethoxy group, and the signal at 1.32–1.29 ppm, which assigned to methyl protons (H_f) of the ethoxy group, clearly indicate the presence of an ethoxy group in the structure of the copolymer obtained.^{10,23} The signal at 5.02 ppm assigned to H_a and the rest two signals at 2.15 and 1.79 ppm assigned to H_b and H_c + H_d according to previous report.^{13f}

It can be deduced from this ¹H NMR spectrum that the copolymerization reaction was initiated by the insertion of CO₂ into a Zn–ethoxy bond of the catalytic species.^{7,10} Thus, the in

situ generated complex **2** probably acts as a catalyst precursor. The alkoxy-containing active species, such as complex **3**, was produced in the reaction of ligand (*S,S*)-**1a** with Et₂Zn reagent followed by the addition of EtOH additive (Scheme 1). Previously mechanistic studies of the catalytic CO₂/epoxide copolymerization reactions also suggested that an alkoxy-containing intramolecular dinuclear zinc complex acted as active species.¹⁰

Nonlinear Effect. To gain insight into the reaction mechanism and confirm the real catalytically active species, a nonlinear effect was also investigated. The copolymerization was performed by treatment of CPO with CO₂ (1 atm) in the presence of a mixture of **1a** (5 mol %), ZnEt₂ (10 mol %), and ethanol (2.0 mol %) to give the completely alternating copolymer. The correlation between the ee values of ligand (*S,S*)-**1a** and ee values of the product PCPC was carefully examined, and the result showed that a positive nonlinear effect was observed in the copolymerization of CPO and CO₂, as depicted in Figure 4.^{7c,24}

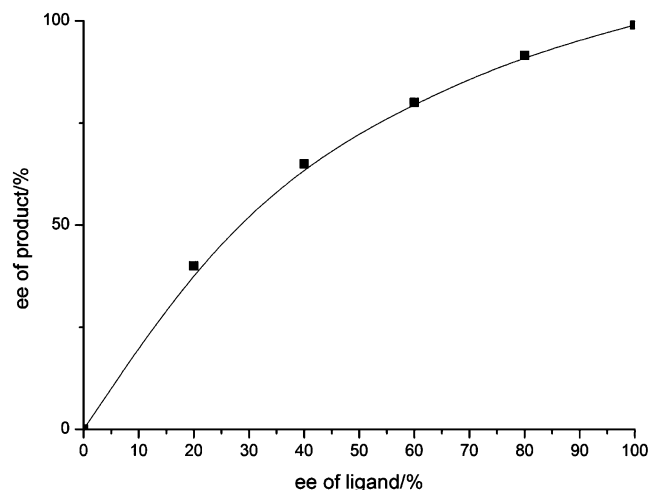
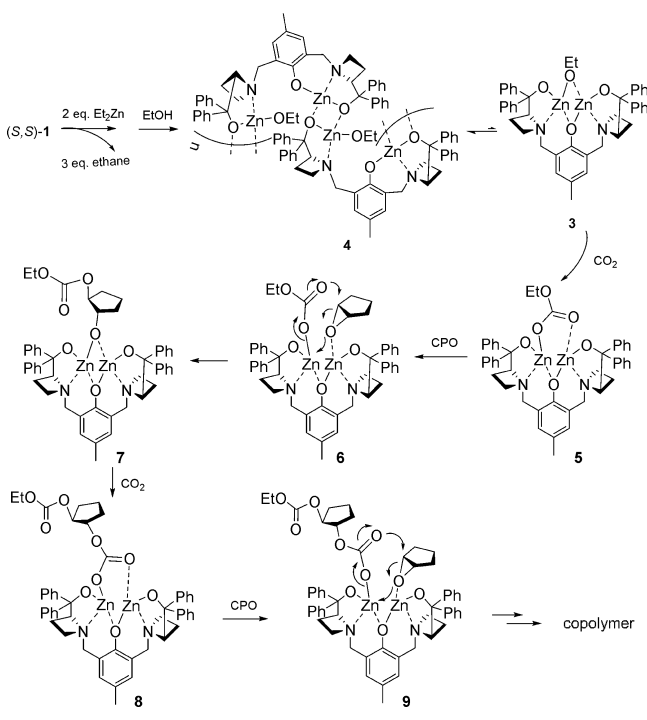


Figure 4. Correlation between the ee values of the ligand (*S,S*)-**1a** and the ee values of product PCPC.

By using optically pure (*S,S*)-**1a** as the chiral ligand, the complex **3** prepared in situ in toluene was soluble. However, a large amount of deposition was observed during the catalyst preparation (see a picture in Supporting Information) when nonenantioselective **1a** was used. As a result, we suppose an intermolecular oligomeric aggregates complex **4** containing two or more monomers are formed prior to monomeric complex **3** when we put the ligand **1a** and two equivalents of ZnEt₂ together in toluene followed by EtOH additive (Scheme 2).^{16,25} And a dynamic balance exists between the complex **3** and complex **4**. Otherwise, there should not be deposition in preparing the racemic catalyst, if monomeric complex **3** is the major complexation form in the dynamic balance.

The positive nonlinear effect suggested that the oligomeric aggregates complex **4** containing two or more monomeric species was catalytically inactive. Thus, the real catalytically active species was complex **3** instead of complex **4**. In addition, the homochiral oligomeric aggregates complex **4** is less stable and more readily disassembled into monomers than heterochiral complex **4** containing both (*S,S*) and (*R,R*) ligands under our reaction conditions, thereby generating a higher concentration of catalytically active monomeric species complex **3**,

Scheme 2. Proposed Catalytic Cycle for the Dinuclear Zinc–AzePhenol Catalyzed Copolymerization of CPO and CO₂



which could further leads to the positive nonlinear effect. This phenomenon is quite similar to most literature examples of intermolecular dimeric metal-complex catalysis.²⁶ Unfortunately, attempts to grow a single crystal of complex 3 or complex 4 were unsuccessful.

EtOH Loading Screening. On the basis of the investigation described above, it has been recognized that the complex 3 might be the major active species in this copolymerization reaction. A change in the concentration of the ethoxide-containing zinc species was expected to have an impact on its catalytic performance. Accordingly, the effect of EtOH additive loading on the catalysis of the copolymerization reaction was also examined. Almost no copolymer was formed in the absence of EtOH under our reaction conditions (Table 2, entry 1). The addition of 1, 2, and 2.5 mol % of EtOH to the in situ prepared complex 2 improved the yields of the copolymers and led to an increase in the molecular weight (Table 2, entries 2–4). Addition of 0.5 equiv (2.5 mol %) of ethanol was found to be optimal, affording the copolymer with a molecular weight of 7 410 g mol^{−1}, (PDI = 1.27) in 97% yield with 99% ee (Table 2, entry 4). However, 3–4 mol % of EtOH led to a decrease in both the yield and the molecular weight (Table 2, entries 5 and 6). When 5 mol % of EtOH was used, almost no PCPC could be obtained (Table 2, entry 7). The enantioselectivity showed no obvious change with the increase of EtOH additive, while the PDI of PCPC became broader and broader (Table 2, entries 2–6).

Those results also indicate that complex 3 might serve as the really catalytically active species in this copolymerization. With the increase of EtOH additive, the concentration of complex 3 was increased which led to the increase of yields and PDI but enantioselectivity.

Given that some amount of ethoxy-containing complex 3 has already been present in the reaction system prior to the addition of any EtOH as reported previously, which was

Table 2. Screening of Additive Loading in the Copolymerization of CPO and CO₂^a

entry	<i>x</i>	yield ^b (%)	<i>M</i> _n ^c (g/mol)	PDI ^c	ee ^d (%)
1	0	<5	<i>e</i>	<i>e</i>	<i>e</i>
2	1	31	2900	1.20	97
3	2	98	3130	1.24	>99
4	2.5	97	7410	1.27	99
5	3	95	7350	1.32	97
6	4	50	5010	1.34	98
7	5	<5	<i>e</i>	<i>e</i>	<i>e</i>

^aUnless otherwise noted, all reactions performed by using 5 mol % ligand (S,S)-1a, 10 mol % ZnEt₂, at 30 °C under 1 atm CO₂ pressure in toluene for 36 h. ^bIsolated yield. ^cEstimated by gel-permeation chromatography analysis by using a polystyrene standard. ^dHydrolyzing the polymer, derivatizing of the resultant diol using benzoyl chloride, and then determining the ee of the dibenzoate by chiral HPLC. ^eNot determined.

generated by an impurity present in the Et₂Zn reagent, probably EtZnOEt,^{7,10,27} it is not surprising that an optimization of the polymerization conditions led to only addition of 2.5 mol % (instead of 5 mol %) of EtOH additive to the in situ generated catalyst precursor complex 2.

Proposed Catalytic Cycle. On the basis of these experimental results and the mechanistic information that dinuclear zinc complex was involved in the transition state of the epoxide ring-opening event during CHO/CO₂ copolymerization reported previously,²⁸ a proposed mechanism that rationalizes the observed sense of asymmetric induction is provided in Scheme 2. Treatment of ligand (S,S)-1a with two equivalents of ZnEt₂ in the presence of 2 mol % EtOH presumably affords catalytically inactive species complex 4 which keeps a dynamic balance with catalytically active species complex 3. Although direct structural evidence for complex 3 could not be ascertained by electrospray mass spectral analysis or X-ray crystallography, previously similar work by Ding and co-workers suggests the formation of a dinuclear zinc complex.¹⁰ Meanwhile, a dinuclear zinc AzePhenol complex could be captured by benzoic acid molecules recently reported by our group.¹⁷

The two zinc centers in complex 3 should be situated sufficiently close to each other to allow a synergistic effect in the copolymerization.¹⁰ That is, one zinc atom activates the CO₂ by the insertion of CO₂ into the Zn–OEt bond affording a carbonate–ester-bridged complex 5, which is the initial step of the copolymerization.^{7,10,29} The other zinc center could activate the epoxide through its coordination. Subsequent nucleophilic attack by the carbonate ester on the back side of the *cis*-epoxide ring in a cooperative manner (6) and the insertion of CO₂ afford the complex 8 with Zn–OP (P, polymer chain). Then the alternating enchainment of CO₂ and CHO completes the catalytic cycle. It is evident that the dinuclear zinc structure of the catalyst remains intact throughout the catalysis of the copolymerization reaction.

CONCLUSION

In summary, we have demonstrated the use of intramolecular dinuclear zinc–AzePhenol catalyst generated in situ in the copolymerization of cyclopentene oxide and CO₂ to afford completely alternating poly(cyclopentene carbonate) with excellent enantioselectivity guided by the DFT calculations. The DFT calculation of the energies of transition states TS_{CPO-re} and TS_{CPO-si} which were the stereoselectivity-determining step and the rate-determining step predicted a high enantioselectivity of 95.3% ee for (S,S)-configuration in the copolymerization of CPO and CO₂ by using complex 3. Experiments were carried out to certify the theoretical calculation results. In the presence of 5 mol % (S,S)-1a, 10 mol % ZnEt₂, and 2 mol % EtOH additive, the copolymerization of CPO and CO₂ can be accomplished under mild conditions at 30 °C under 1 atm pressure of CO₂ affording completely alternating copolymers PCPC in 98% yield with >99% enantioselectivity for (S,S)-configuration, which offers a promising alternative strategy for the synthesis of chiral cyclopentane-1,2-diol. It was recognized that the real catalytically active species was complex 3 according to the structure analysis of PCPC and the positive nonlinear effect study in this copolymerization. Meanwhile, a plausible mechanism was tentatively put forward to explain the origin of the asymmetric induction. Future work will be focused on determining the precise structures of active species as well as the extension of this catalyst system to other epoxides/CO₂ copolymerization reactions.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and analytical data for all new compounds. 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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