

Asymmetric Alternating Copolymerization of Cyclohexene Oxide and CO₂ with Dimeric Zinc Complexes

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Abstract: Dimeric zinc complex **2a** [$= \text{Et}_2\text{Zn}_2(\mathbf{1a})_2$] has been synthesized by the reaction of Et_2Zn and (*S*)-diphenyl(pyrrrolidin-2-yl)methanol (**1a-H**). X-ray crystallography revealed that the alkoxide ligand replaced one of the two ethyl groups of Et_2Zn and formed a five-membered chelate ring through a Zn–N dative bond. Two zinc centers were bridged by oxygen atoms to form a Zn_2O_2 four-membered ring with a syn relationship between the two ethyl groups on the zinc centers. Dimeric zinc complex **2a** was an active catalyst for asymmetric alternating copolymerization of cyclohexene oxide and CO₂. An MALDI-TOF mass spectrum of the obtained copolymer showed that the copolymerization was initiated by the insertion of CO₂ into Zn–alkoxide to give [(*S*)-diphenyl(pyrrrolidin-2-yl)methoxy]–[C(=O)O–(1,2-cyclohexylene)–O]_n–H (copolymer **I**), including chiral ligand **1a** as an initiating group. Complex **3a-OEt** ($= \text{EtZn}(\mathbf{1a})_2\text{ZnOEt}$), in which an ethoxy group replaced one of the two ethyl groups in **2a**, also polymerized cyclohexene oxide and CO₂ with higher catalytic activity and enantioselectivity than **2a** and afforded $\text{EtO}–[\text{C}(=\text{O})\text{O}–(1,2\text{-cyclohexylene})–\text{O}]_n–\text{H}$ ($=$ copolymer **III**), including an ethoxy group as an initiating group. Throughout the studies, dimeric zinc species are indicated to be the active species for the copolymerization. It is also depicted that the substituent on the aryl moiety in diaryl(pyrrrolidin-2-yl)methanol **2b–e** influenced the polymerization activity.

Introduction

In the past decades, synthetic chemists have discovered a variety of asymmetric catalysts which can convert prochiral small molecules into chiral compounds with enantioenriched forms, indispensable for the synthesis of pharmaceuticals, agrochemicals, and other fine chemicals.¹ A small amount of chiral catalyst repeatedly activates prochiral molecules and controls the stereochemistry to give a large amount of optically active molecules. When such a powerful synthetic strategy is applied to polymerization, optically active polymers with main-chain chirality can be produced from optically inactive, prochiral monomers. This type of polymerization reaction is classified into asymmetric synthesis polymerization and is attracting much attention as one of the more efficient and economical methods for accessing optically active polymers which are considered as candidates for new and valuable materials.² Some accomplished examples in asymmetric synthesis polymerization

are polymerization of conjugated 1,3-dienes³ or cyclic olefins,⁴ cyclopolymerization of dienes,⁵ copolymerization of α -olefins with carbon monoxide,⁶ and Diels–Alder polymerization of a bisdienophile monomer with a bisdiene monomer.⁷ These achievements are the fruits of fine organic synthesis.

In the course of our studies on asymmetric synthesis polymerization, we considered a possibility of asymmetric alternating copolymerization of *meso*-epoxide with CO₂. Since the first report by Inoue and Tsuruta on the alternating copolymerization of epoxides and CO₂,⁸ intensive studies have been directed to the copolymerization, and a significant advance

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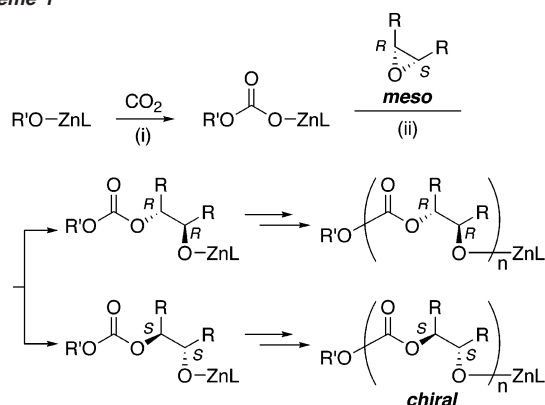
[‡] Japan Science and Technology Corporation.

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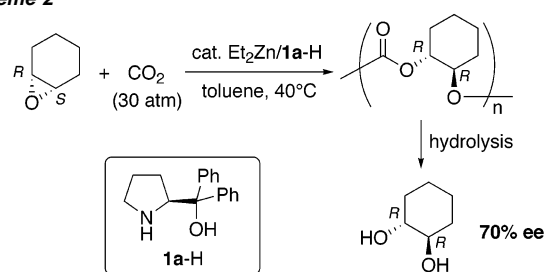
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Scheme 1

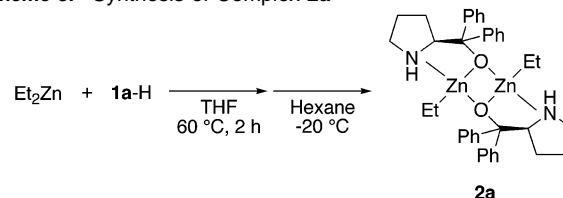


in catalytic activity has been achieved in the (last decade by use of well-defined metal complexes as catalysts or supercritical CO₂ as a solvent.^{9–14} Accepted reaction mechanisms are (i) the CO₂ insertion into Zn–alkoxide bond and (ii) the ring-opening of epoxide by backside attack of the resulting carbonate (Scheme 1).^{11,13,15,16} 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 can give optically active aliphatic polycarbonate with an (*R,R*)- or (*S,S*)-*trans*-1,2-diol unit. From the viewpoint that a chiral catalyst does not create new chiral centers but selects one of the chiral centers of *meso*-compounds, this *meso*-desymmetrizing polymerization differs from the asymmetric synthesis polymerization with olefinic compounds as monomers. Although such a concept of enantioselective desymmetrization of *meso*-materials is an attractive and extremely powerful method in asymmetric synthesis,¹⁷ there have been few cases of the application to asymmetric polymerization.¹⁸ In 1999, we reported the first example of the asymmetric alternating copolymerization of *meso*-epoxide and CO₂ (Scheme 2).¹⁹ Optically active poly-[cyclohexene oxide-*alt*-CO₂] (70% ee) was obtained by using

Scheme 2



Scheme 3. Synthesis of Complex 2a



an equimolar mixture of Et₂Zn and (*S*)-diphenyl(pyrrolidin-2-yl)methanol (**1a-H**) as a chiral catalyst. The determination of the degree of asymmetric induction on the resulting copolymer was performed by a unique method. Polycarbonate can be easily hydrolyzed into *trans*-1,2-diol and CO₂ by alkali-treatment, which enables us to evaluate the degree of asymmetric induction unambiguously.²⁰ This is in contrast with the conventional studies on asymmetric synthesis polymerization which relied on the measurement of optical rotation which has, in most cases, no information on stereochemical purity. In 2000, Coates et al. reported asymmetric alternating copolymerization with the well-defined Zn-imine oxazoline ligand (IOx) complex, which showed higher activity under mild conditions and controlled molecular weight.²¹

In our previous report, we used a zinc complex generated in situ, not isolated, and had little information about the real active species. Here, we describe the isolation and the solid-state characterization of Et₂Zn-amino alcohol complex **2a**. This complex has a dimeric structure and can catalyze the asymmetric copolymerization of cyclohexene oxide and CO₂. Determination of a polymer end group (initiating group) was achieved by MALDI-TOF mass spectroscopy, which gave us an insight into developing the Zn-amino alcohol complex with higher catalytic activity and enantioselectivity. Addition of an alcohol to dimeric zinc complex **2a** improved the catalytic activity and enantioselectivity. The zinc catalyst is indicated to maintain a dimeric structure in the polymerization.

Results and Discussion

Synthesis and Characterization of Dimeric Zinc Complex 2a

(*S*)-Diphenyl(pyrrolidin-2-yl)methanol (**1a-H**) was synthesized using the procedure reported by Corey et al.²² The zinc complex **2a** was obtained as a single crystal by treatment of Et₂Zn with 1 equiv of **1a-H** in THF at 60 °C for 2 h, followed by recrystallization from THF/hexane at –20 °C (Scheme 3). X-ray single-crystal diffraction revealed that the obtained zinc complex **2a** formed a dimeric structure in which two zinc centers were coordinated in a distorted tetrahedral geometry, as il-

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- (20) For an example of the optical purity determination of the polymer with main-chain chirality by degrading into chiral repeating units, see ref 7a. (21) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007. (22) Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1989**, *30*, 6275.

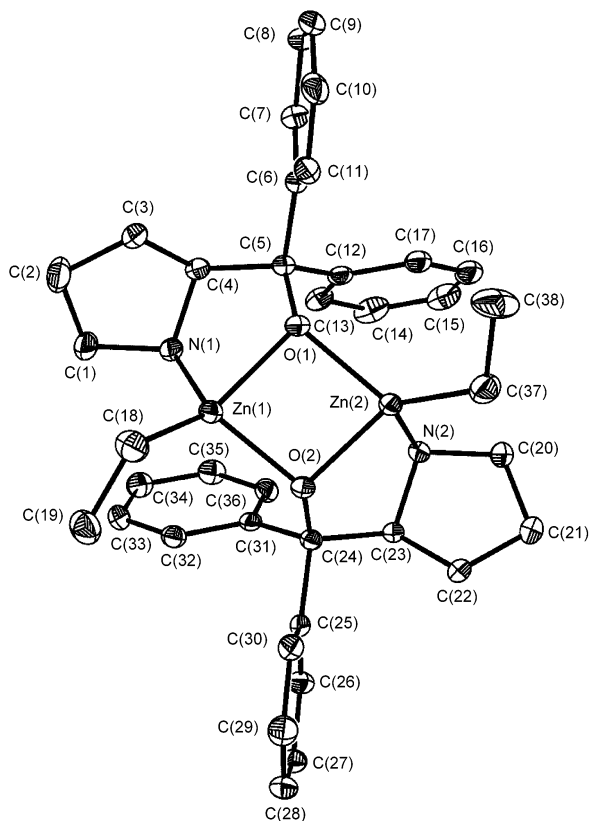


Figure 1. ORTEP drawing of complex **2a** with thermal ellipsoids shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

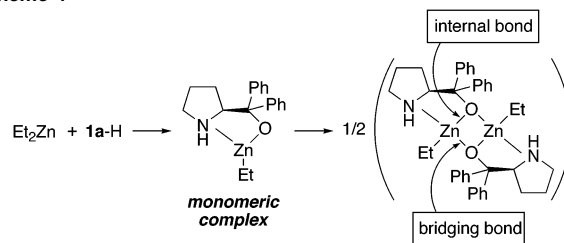
Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complex **2a**

Bond Distances			
Zn(1)–O(1)	2.0382(15)	Zn(2)–O(2)	2.0301(15)
Zn(1)–O(2)	2.0242(15)	Zn(2)–O(1)	2.0355(15)
Zn(1)–N(1)	2.1357(18)	Zn(2)–N(2)	2.1560(19)
Zn(1)–C(18)	1.987(2)	Zn(2)–C(37)	1.987(2)
Bond Angles			
O(1)–Zn(1)–O(2)	84.22(6)	O(2)–Zn(2)–O(1)	84.14(6)
O(1)–Zn(1)–N(1)	81.30(6)	O(2)–Zn(2)–N(2)	80.43(7)
O(1)–Zn(1)–C(18)	131.64(8)	O(2)–Zn(2)–C(37)	133.68(9)
O(2)–Zn(1)–N(1)	116.11(7)	O(1)–Zn(2)–N(2)	117.90(6)
O(2)–Zn(1)–C(18)	114.81(9)	O(1)–Zn(2)–C(37)	118.07(8)
N(1)–Zn(1)–C(18)	120.97(9)	N(2)–Zn(2)–C(37)	115.72(9)

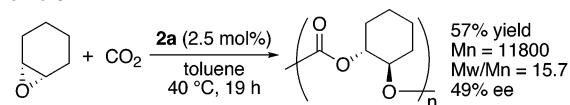
illustrated in Figure 1 and Table 1. Diethyl zinc reacted with **1a-H** to form a tricoordinate monomeric zinc complex in which one of the two ethyl groups of Et_2Zn was replaced with **1a** and another one remained on the zinc center without reacting with an NH group (Scheme 4).²³ The nitrogen atom coordinated to a zinc atom to form a prolinol-Zn five-membered chelate ring (the O–Zn bond in this chelate ring is named as an internal bond). Then, this coordinatively unsaturated monomeric zinc complex dimerized to dimeric zinc complex **2a** through the two bridging O–Zn bond to form a Zn_2O_2 four-membered ring. The two ethyl groups on the zinc centers of **2a** are oriented in a syn fashion, which is common to the dimer of $\text{R}_2\text{Zn}(-)-\text{DAIB}$.^{24,25} In complex **2a**, the bridging O(1)–Zn(2) bond (2.036

(23) In our previous communication, both of the ethyl groups of Et_2Zn were reported to be protonated with –OH and –NH groups, based on the disappearance of the ^1H NMR signals assigned to ethyl group when 1.0 equiv of **1a-H** was added to Et_2Zn in hexane–toluene- d_8 at 20 °C. The disappearance of the signals may result from the overlapping with other signals or the signal broadening.

Scheme 4



Scheme 5



Å) and O(2)–Zn(1) bond (2.024 Å) were very close to the internal O(1)–Zn(1) bond (2.038 Å) and O(2)–Zn(2) bond (2.030 Å), respectively. Such a relationship between the bridging O–Zn and the internal O–Zn bond lengths of complex **2a** is in contrast to that in the case of the $\text{Me}_2\text{Zn}(-)-\text{DAIB}$ complexes.²⁴ In the $\text{Me}_2\text{Zn}(-)-\text{DAIB}$ complexes, the bridging O–Zn bonds were 4% longer than the internal O–Zn bonds. Based on such a context, the very small difference between the bridging O–Zn bonds and the internal O–Zn bonds in complex **2a** indicates the high degree of electron delocalization in the Zn_2O_2 four-membered ring, contributing to stabilization of the dimer form.

Copolymerization of Cyclohexene Oxide and CO_2 with Dimeric Zinc Complex **2a.** We investigated the ability of the isolated complex **2a** to initiate and catalyze the copolymerization of cyclohexene oxide and CO_2 . In an autoclave containing a toluene solution of dimeric zinc complex **2a** and cyclohexene oxide (cyclohexene oxide/**2a** = 40), the copolymerization was initiated by introducing 30 atm of CO_2 at 40 °C to give the completely alternating copolymer in 57% yield with an M_n value of 11 800 and a large M_w/M_n ratio of 15.7 (Scheme 5). The completely alternating structure was verified by no observable signal assignable to the repeating oxy(1,2-cyclohexene) unit (δ 3.4 ppm, ether linkage) in the ^1H NMR spectrum of the resulting copolymer.²⁶ Hydrolysis of the copolymer gave a *trans*-1,2-cyclohexane diol of 49% ee [(*R,R*)/(*S,S*) = 74.5/25.5] in an almost quantitative yield. Thus, dimeric zinc complex **2a** was found to be active for the asymmetric alternating copolymerization of cyclohexene oxide and CO_2 , while catalytic activity and enantioselectivity were lower than those (>99% yield, 70% ee) with a mixture of Et_2Zn and **1a-H** reported in our communication (*vide infra*).¹⁹

The completely alternating structure of the copolymer enabled the determination of an end group by MALDI-TOF mass

- (24) Dimeric zinc complexes from Me_2Zn and a β -amino alcohol: (a) Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028. (b) Kitamura, M.; Suga, S.; Niwa, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 4832. (c) Kitamura, M.; Yamakawa, M.; Oka, H.; Suga, S.; Noyori, R. *Chem.–Eur. J.* **1996**, *2*, 1173.
- (25) The solid-state structures of other dimeric zinc complexes [$\text{RZn}(\text{L})_2$] (L = chiral monoanionic chelate ligand) were also characterized by X-ray analysis. See the following references. Aminothiolato ligand: (a) Rijnberg, E.; Jastrzebski, J. T. B. H.; Jassen, M. D.; Boersma, J.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 6521. (b) Rijnberg, E.; Hovestad, N. J.; Kleij, A. W.; Jastrzebski, J. T. B. H.; Boersma, J.; Jassen, M. D.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 2847. Aminoalkolato ligand: Mimoun, H.; Laumer, J. Y. S.; Giannini, L.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 6158. Pyridylalkolato ligand: Bolm, C.; Schlingloff, G.; Harms, K. *Chem. Ber.* **1992**, *125*, 1191.
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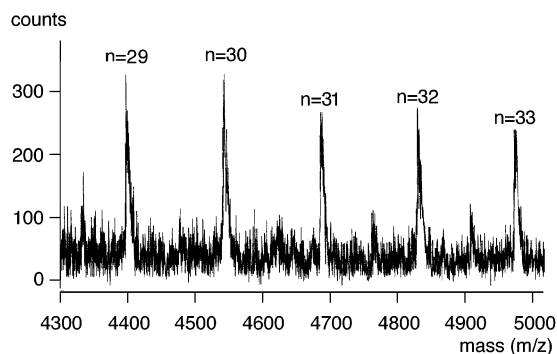


Figure 2. MALDI-TOF mass spectrum of the copolymer obtained with complex **2a**.

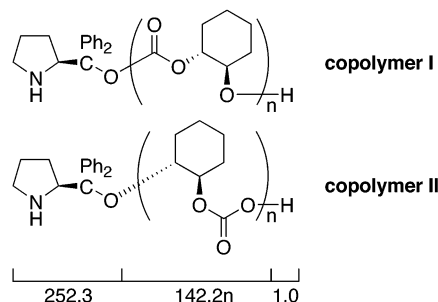


Figure 3. Structures of copolymer **I** and **II**.

spectroscopy, which gave us valuable information about the polymerization mechanism.²⁷ Figure 2 shows the mass spectrum of the copolymer produced with **2a**. This spectrum was obtained with 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol) as a matrix and sodium trifluoroacetate as a cationizing agent. In the mass spectrum, only one series of signals with regular intervals of 142.2 (repeating unit) could be observed, and the mass number of each signal matches $[142.2n$ (repeating unit) + 252.3 (**1a**) + 1.0 (H) + 23.0 (Na^+ ion)]. This result shows that copolymerization was initiated by **1a** on a zinc center and terminated by protolysis to give either copolymer **I** or **II** (Figure 3). The difference between copolymer **I** and **II** is attributed to the two possible initiation mechanisms: (i) the insertion of CO_2 into a Zn–alkoxide bond of **2a** to initiate the copolymerization affording copolymer **I** or (ii) the ring-opening of epoxide by the nucleophilic attack of alkoxide in **2a** to start the copolymerization giving copolymer **II**. Judging from the instability of carbonic acid monoester which is a terminal group of copolymer **II**, we conclude that copolymer **I** is the reasonable structure and the initiation reaction should be the CO_2 insertion into the Zn–alkoxide bond of **2a**. The dissociation of chelating ligand **1a** required such a high energy that the initiation reaction did not occur at the same time, which may have caused the large polymer weight distribution of the copolymer.^{11d}

The determination of a polymer end group poses a question of how asymmetric induction was achieved to give the optically active copolymer of 49% ee despite the dissociation of a chiral ligand from the catalytically active zinc center after the initiation reaction. This may explain the participation of a dimeric zinc species in the copolymerization process, as was also mentioned in precedent reports.²⁸ A possible reaction mechanism is

Scheme 6. A Possible Reaction Mechanism Initiated by Complex **2a**

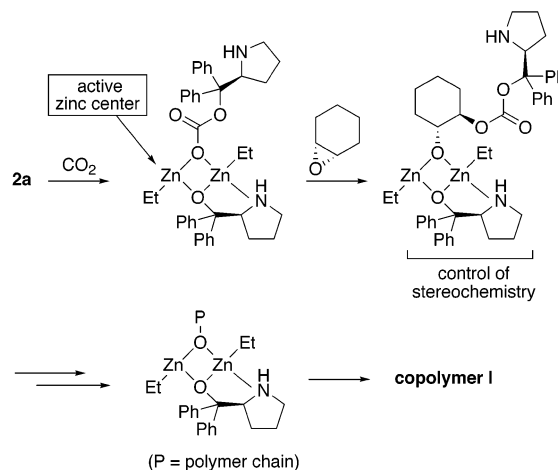


Table 2. Copolymerization of Cyclohexene Oxide and CO_2 with a Mixture of Complex **2a** and Ethanol^a

run	EtOH (equiv to 2a)	yield (%) of polymer ^b	M_n (M_w/M_n) ^c	% ee ^d (<i>R,R</i>)
1 ^e	0.0	57	11800 (15.7)	49
2	0.2	94	12300 (7.18)	64
3	0.4	95	12000 (1.30)	74
4	0.6	>99	9900 (1.39)	72
5	0.8	91	6300 (1.43)	75
6	1.0	71	4500 (1.82)	76
7	2.0	trace		

^a Cyclohexene oxide (10 mmol) was treated with CO_2 (30 atm) in the presence of a mixture of the zinc complex **2a** (0.25 mmol) and a desirable amount of EtOH in toluene (17 mL) at 40 °C for 19 h. ^b Calculated based on cyclohexene oxide. ^c Estimated by size-exclusion chromatography analysis using a polystyrene standard. ^d Determined based on the enantiomeric excess of a *trans*-1,2-cyclohexane diol given after hydrolysis of copolymer. ^e The same as Scheme 5.

illustrated in Scheme 6. During the polymerization, a monomeric zinc species possibly interacts with the active zinc center through coordination of the oxygen atom; that is, the monomeric zinc species works as a chiral ligand. Consequently, the remaining chiral ligand **1a** is able to control the enantioselectivity of the ring-opening of epoxide.

Improvement of the Catalytic Activity and Enantioselectivity: Effect of Addition of an Alcohol to Complex 2a. While, as mentioned previously, asymmetric alternating copolymerization was achieved by use of dimeric zinc complex **2a**, ligand dissociation from the catalytic center would have diminished the degree of asymmetric induction. To realize the inhibition of the ligand dissociation, we added an alcohol to complex **2a**: additional alcohol should replace (an) ethyl group(s) on the zinc centers to give (a) new Zn–OR bond(s), so that copolymerization would be initiated not by the chiral ligand **1a** but by the resulting alkoxide ligand.

Copolymerization of cyclohexene oxide and CO_2 was carried out with a mixture of complex **2a** and varying amounts of ethanol, as summarized in Table 2. Addition of 0.2–0.8 equiv of ethanol to **2a** improved the chemical yield quantitatively and enantioselectivity to almost up to 75% and achieved the control of molecular weight (runs 2–5). Addition of 1.0 equiv of ethanol resulted in a slight decrease in catalytic activity (71% yield),

(27) For reviews on mass spectrometry of synthetic polymers, see: (a) Nielen, M. W. *Mass Spectrom. Rev.* **1999**, *18*, 309. (b) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527.

(28) Kuran, W.; Listos, T. *Macromol. Chem. Phys.* **1994**, *195*, 401. (b) Kuran, W.; Listos, T. *Macromol. Chem. Phys.* **1994**, *195*, 977. (c) Listos, T.; Kuran, W.; Siwiec, R. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 393.

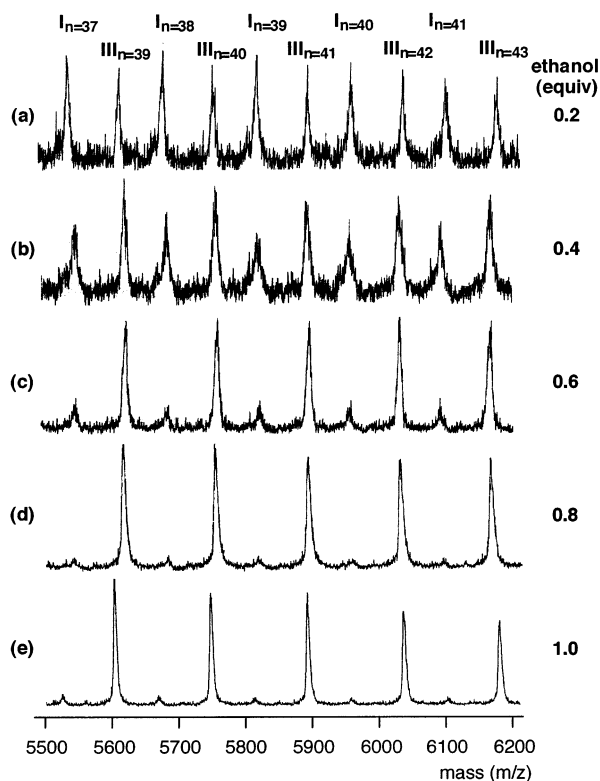


Figure 4. MALDI-TOF mass spectra of the copolymers obtained with a mixture of complex **2a** and 0.2–1.0 equiv of ethanol (a–e). The signals assigned to copolymer **I** and **III** were represented by I_n and III_n , respectively.

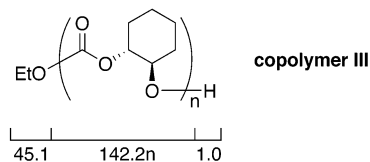


Figure 5. Structure of copolymer **III** with an ethoxy group as an initiating group.

although enantioselectivity was maintained (76% ee) (run 6). However, addition of 2.0 equiv of ethanol caused the drastic decrease of catalytic activity (run 7).

The introduction of an ethoxy end group was confirmed by MALDI-TOF mass spectra of the obtained copolymers (Figure 4). Besides the series of signals assigned to the amino alcohol-attached copolymer **I**, we observed another series of signals with regular intervals of 142.2 when 0.2 equiv of ethanol was added (Figure 4a). With the increase of the amount of additional ethanol, this new series of signals grew in intensity, whereas the signals of copolymer **I** diminished (Figure 4b–e). The mass number of the new signals matched $[142.2n$ (repeating unit) + 45.1 (EtO) + 1.0 (H) + 23.0 (Na⁺ ion)] and can be assigned to copolymer **III** bearing an ethoxy group as the initiating group (Figure 5). The structure of copolymer **III** initiated by the Zn–OEt complex was also confirmed by the ¹H NMR spectrum of the produced copolymer (Figure 6). The signal assigned to methylene protons (a) of the ethoxy group was observed at 4.18 ppm (quartet), which did not appear in the ¹H NMR spectrum of copolymer **I**. Two small signals at 4.40 and 3.58 ppm were assignable to methine protons (c, d) in the terminal hydroxy-(1,2-cyclohexylene) group.²⁹

One possible explanation for the effect of ethanol is a reaction mechanism involving dimeric zinc complex **3a-OEt**, as shown

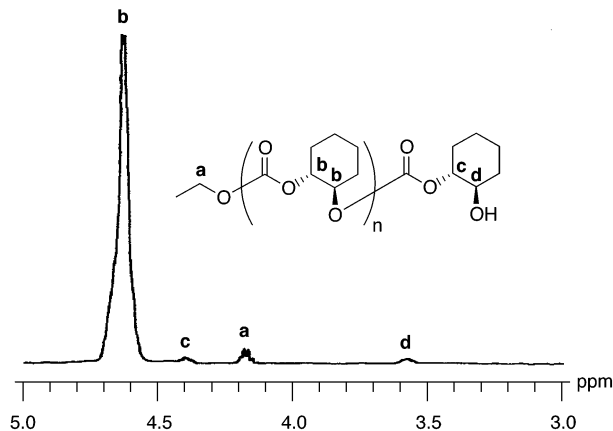
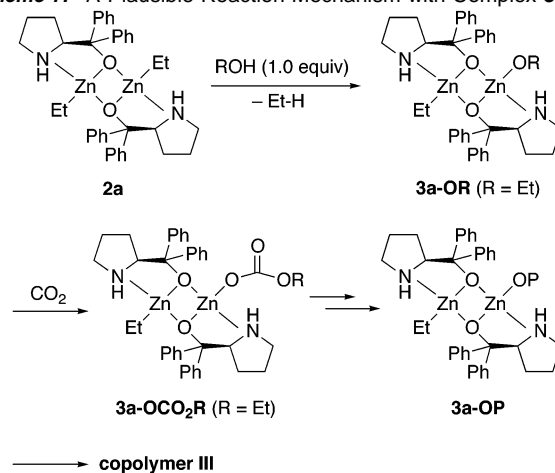


Figure 6. ¹H NMR spectrum of the copolymer of cyclohexene oxide and CO₂ with use of a **2a**–ethanol (0.8 equiv) system at 40 °C (500 MHz, CDCl₃).

Scheme 7. A Plausible Reaction Mechanism with Complex **3a**

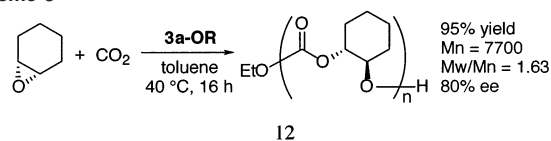


in Scheme 7. Copolymerization is initiated by CO₂ insertion into the Zn–OEt bond of dimeric zinc complex **3a-OEt**, which has an ethoxy group on one zinc center and an ethyl group on the other zinc center. The active zinc center in the resulting complex **3a-OCO₂Et** is coordinated in a tetrahedral geometry and has no epoxide binding site, although it was reported in the literature that one epoxide binding site was necessary for the epoxide ring-opening.^{11c} Accordingly, one of the two oxygen atoms or the nitrogen atom attached to the active zinc center may have worked as a hemi-labile ligand. Subsequent ring-opening of epoxide and the insertion of CO₂ afford complex **3a-OP** (P, polymer chain) which is converted to copolymer **III** after hydrolysis. Because of lack of chelate stabilization, CO₂ insertion into the Zn–OEt bond in **3a-OEt** is faster than that into Zn–amino alkoxide **1a** to give copolymer **III** selectively, and complex **3a-OEt** can catalyze the copolymerization minimizing the dissociation of the chiral ligands. The lowered molecular weight distribution also indicates the smooth initiation reaction by a Zn–OEt complex. Thus, higher catalytic activity, lower M_w/M_n and higher stereocontrol have been realized with **3a-OEt**.³⁰

Here, it is anticipated whether, prior to the copolymerization, dimeric zinc complex **3a-OEt** dissociated into monomeric zinc complexes EtZn(**1a**) and EtOZn(**1a**) which would have been

(29) Nakano, K.; Nozaki, K.; Hiyama, T. *Macromolecules* **2001**, *34*, 6325.

Scheme 8



given by the dissociation of Et₂Zn₂(1a)₂ (= 2a) and (EtO)₂Zn₂(1a)₂, respectively. However, the involvements of these two monomeric complexes EtZn(1a) and EtOZn(1a) in the copolymerization are less plausible based on the experimental results that (i) copolymer I which was produced by 2a was hardly formed when 0.8–1.0 equiv of ethanol was added to 2a and that (ii) the addition of 2.0 equiv of ethanol to 2a, which would have converted 2a to (EtO)₂Zn₂(1a)₂, was inert for the copolymerization.

Ideally, addition of 1.0 equiv of ethanol would transform 2a to 3a-OEt quantitatively, although the optimum conditions of in situ generation of 3a-OEt are accomplished by the addition of 0.8 equiv of ethanol to 2a. To isolate the pure complex 3a-OEt, reprecipitation of the product given by the reaction of complex 2a with 0.5 equiv of ethanol was performed from THF/hexane to yield a colorless solid, unsuitable for X-ray analysis. This obtained zinc complex was shown to be a good catalyst to afford the completely alternating copolymer of 80% ee, the highest enantiomeric excess ever reported (Scheme 8). Differential scanning calorimetry of the copolymer showed glass transition temperature (*T*_g) at 117 °C, the value being very close to the ones previously reported for the copolymers with a lower stereoregularity.^{21,31}

As we previously reported, the mixture of Et₂Zn and 1a-H produced a copolymer of 70% ee,¹⁹ while the isolated complex 2a gave the copolymer of only 49% ee (Table 2, run 1). The difference may have resulted from the impurity of Et₂Zn, probably EtZn-OEt; in other words, the reaction mixture of Et₂Zn and 1a-H might have contained both 2a and 3a-OEt. In fact, the MALDI-TOF mass spectrum of the copolymer obtained with the Et₂Zn/1a-H mixture exhibited two series of signals assignable to copolymer I and III.³²

Relationship between the Monomer Conversion and the Number Average Molecular Weight. A plot of molecular weight and polydispersity of the copolymer versus conversion of cyclohexene oxide is shown in Figure 7 for the copolymerization with in situ generated 3a-OEt (Table 3). As the copolymerization reaction proceeded, a linear increase of molecular weight was observed. Furthermore, the copolymers at each conversion showed unimodal elution curves in the GPC chromatogram and a relatively narrow polydispersity. These results indicated the living nature of the copolymerization of cyclohexene oxide and CO₂ with 3a-OEt.

Alcohol Effect. To test the effect of the initiating alkoxide, several alcohols were examined in combination with complex 2a, and the results are listed in Table 4. Copolymerization proceeded in good yields and with high stereoselectivity to give

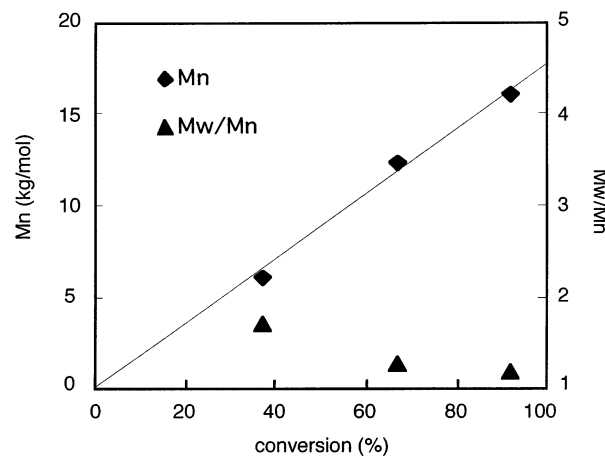


Figure 7. Plot of molecular weight (M_n) and polydispersity (M_w/M_n) of the copolymer as a function of the conversion of cyclohexene oxide using a mixture of 2a and 0.8 equiv of EtOH (cyclohexene oxide/2a = 120).

Table 3. Relationship between Monomer Conversion and the Resulting Copolymer^a

conversion (%) of cyclohexene oxide ^b	isolated yield (%) of polymer ^c	M_n (M_w/M_n) ^d	% ee (<i>R,R</i>) ^e
37	36	6100 (1.70)	74
67	68	12300 (1.26)	73
92	88	16100 (1.19)	70

^a Cyclohexene oxide (30 mmol) was treated with CO₂ (30 atm) in the presence of a mixture of the zinc complex 2a (0.25 mmol) and EtOH (0.20 mmol) in toluene (17 mL) at 40 °C. ^b Determined by GC analysis. ^c Calculated based on cyclohexene oxide. ^d Estimated by size-exclusion chromatography analysis using a polystyrene standard. ^e Determined based on the enantiomeric excess of a *trans*-1,2-cyclohexane diol given after hydrolysis of copolymer.

Table 4. Effects of Alcohols: Copolymerization with a Mixture of 2a and Various Alcohols, ROH^a

run	ROH	yield (%) of polymer ^b	M_n (M_w/M_n) ^c	% ee (<i>R,R</i>) ^d
1 ^e	EtOH	91	6300 (1.43)	75
2	MeOH	99	8400 (1.50)	75
3	BnOH	91	4100 (2.23)	74
4	^t PrOH	97	5000 (1.85)	78
5	^t BuOH	99	6500 (1.49)	78
6	CF ₃ CH ₂ OH	86	6800 (1.58)	60

^a Cyclohexene oxide (10 mmol) was treated with CO₂ (30 atm) in the presence of a mixture of the zinc complex 2a (0.25 mmol) and ROH (0.20 mmol) in toluene (17 mL) at 40 °C for 19 h. ^b Calculated based on cyclohexene oxide. ^c Estimated by size-exclusion chromatography analysis using a polystyrene standard. ^d Determined based on the enantiomeric excess of a *trans*-1,2-cyclohexane diol given after hydrolysis of copolymer. ^e The same as run 5 of Table 2.

the copolymer bearing the added alcohol as the initiating group. For each case, the introduction of added alcohol into the polymer-chain end was ascertained by MALDI-TOF mass spectra.³³ These results suggest that the copolymerization was initiated by CO₂ insertion into 3a-OR to form complex 3a-OCO₂R, as was the case for ethanol. After the initiation reaction, the same species (zinc-carbonate complex) should be generated to catalyze the following polymerization.

A slight decrease of activity and enantioselectivity was observed by the addition of trifluoroethanol. In addition, three series of copolymers were detected by mass spectrum; these are copolymer I with an amino alkoxide 1a as an initiating

(33) See Supporting Information.

(30) Recently, Coates and co-workers have reported that the copolymerization of cyclohexene oxide with CO₂ initiated by [Zn(OR)(BDI)]₂ complexes are second order in [Zn(OR)(BDI)], which suggests the participation of di-zinc species in the enchainment of monomer. See ref 13c. At present, the possibility for the further aggregation of 3a-OR cannot be omitted.

(31) Koning, C.; Wildeson, J.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. *Polymer* **2001**, *42*, 3995.

(32) We checked that copolymerization with an equimolar mixture of carefully stored Et₂Zn and 1a-H afforded the copolymer of 55% ee in 67% yield. This result was almost the same when isolated complex 2a was used.

Scheme 9

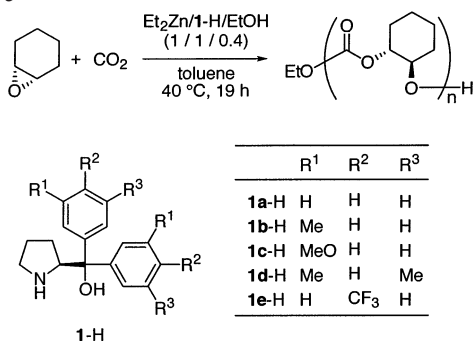


Table 5. Effects of Ligands: Copolymerization with a Mixture of Et₂Zn, (*S*)-Diaryl-pyrrolidin-2-yl-methanols **1(a–e)-H**, and EtOH^a

amino alcohol	yield (%) of polymer ^b	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^c	% ee (<i>R,R</i>) ^d
1a-H	99	6400 (1.43)	77
1b-H	99	7200 (1.37)	64
1c-H	99	4400 (1.98)	45
1d-H	74	3700 (1.56)	racemic
1e-H	34 ^e	12700 (32)	3

^a Cyclohexene oxide (10 mmol) was treated with CO₂ (30 atm) in the presence of a mixture of Et₂Zn (0.50 mmol), **1** (0.50 mmol), and EtOH (0.20 mmol) in toluene (17 mL) at 40 °C for 19 h. ^b Calculated based on cyclohexene oxide. ^c Estimated by size-exclusion chromatography analysis using a polystyrene standard. ^d Determined based on the enantiomeric excess of a *trans*-1,2-cyclohexane diol given after hydrolysis of copolymer. ^e [carbonate linkage]/[ether linkage] = 4.6/1.

group, a copolymer initiated by CO₂ insertion into the Zn–OCH₂CF₃ bond, and a copolymer initiated by the ring-opening of epoxide. Possibly, lower nucleophilicity of CF₃CH₂O[−] led amino alkoxide ligand **1a** into initiating the reaction to give copolymer **I**, and the electron-withdrawing nature of a trifluoromethyl group made the zinc center of the complex **3a-OCH₂CF₃** more electron deficient so that the efficient epoxide coordination was accomplished to favor the ring-opening of epoxide as the initiation step.

Ligand Effect. Catalytic activities depended greatly on the substituents on the phenyl group of **1a**. All (*S*)-diaryl(pyrrolidin-2-yl)methanols (**1b–e**)-H were synthesized using the same procedure as described for **1a-H** with the corresponding aryl-magnesium bromide.³⁴ All copolymerization reactions were carried out using the zinc complexes generated in situ by the reaction of Et₂Zn, **1-H**, and EtOH (1/1/0.4) (Scheme 9),³⁵ and the results are summarized in Table 5. While monosubstitution at the *meta*-position (**1b**, **1c**) resulted in a slight loss of enantiomeric excess of copolymers, other ligands (substitution at both of the *meta*-positions (**1d**) or at the *para*-position (**1e**)) resulted in a significant decrease of catalytic activity and enantioselectivity. Particularly, when *p*-trifluoromethyl substituted ligand **1e-H** was used, the continuous ring-opening of epoxide was facilitated to give the nonalternating copolymer with ether linkages in addition to carbonates. This may have been caused by the electron-withdrawing nature of the trifluoromethyl group, making the zinc centers more acidic to activate an epoxide more strongly. The trifluoromethyl group also affected the crystal structure of the Et₂Zn₂(**1e**)₂ complex (**2e**).

(34) Mathre, D. J.; Jones, T. K.; Xavier, L. C.; Blacklock, T. J.; Reamer, R. A.; Mohan, J. J.; Jones, E. T. T.; Hoogsteen, K.; Baum, M. W.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 751.

(35) Except for **1f**, recrystallization from the reaction mixture of Et₂Zn and **1** did not give the suitable single crystals for X-ray analysis.

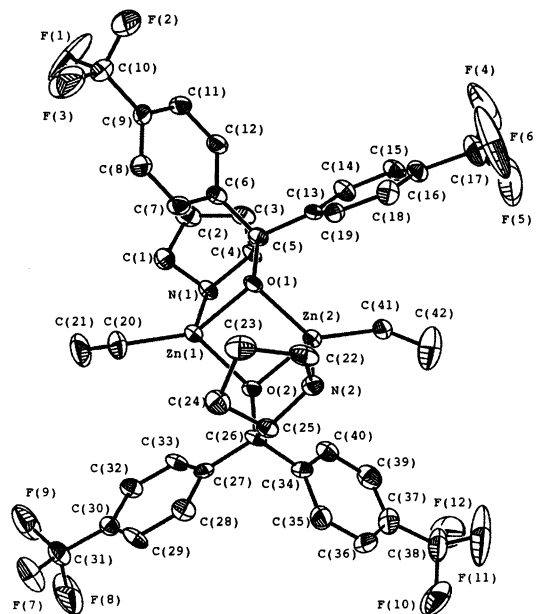


Figure 8. ORTEP drawing of complex **2e** with thermal ellipsoids shown at the 50% probability level. All hydrogen atoms and toluene molecules are omitted for clarity.

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for Complex **2e**

Bond Distances			
Zn(1)–O(1)	2.048(3)	Zn(2)–O(2)	2.041(3)
Zn(1)–O(2)	2.035(3)	Zn(2)–O(1)	2.030(3)
Zn(1)–N(1)	2.126(4)	Zn(2)–N(2)	2.139(4)
Zn(1)–C(20)	1.990(5)	Zn(2)–C(41)	1.994(5)
Bond Angles			
O(1)–Zn(1)–O(2)	84.26(12)	O(2)–Zn(2)–O(1)	84.58(12)
O(1)–Zn(1)–N(1)	80.14(14)	O(2)–Zn(2)–N(2)	82.40(14)
O(1)–Zn(1)–C(20)	133.6(2)	O(2)–Zn(2)–C(41)	130.00(19)
O(2)–Zn(1)–N(1)	102.97(15)	O(1)–Zn(2)–N(2)	103.99(15)
O(2)–Zn(1)–C(20)	126.6(2)	O(1)–Zn(2)–C(41)	128.85(17)
N(1)–Zn(1)–C(20)	117.4(2)	N(2)–Zn(2)–C(41)	115.5(2)

As depicted in Figure 8, **2e** had a dimeric structure where the two ethyl groups on the zinc centers were oriented in an anti fashion, which was contrastive to the structure of complex **2a**. The two bridging O–Zn bonds (O(1)–Zn(2), 2.030 Å; O(2)–Zn(1), 2.035 Å) were very close to the internal O–Zn bonds (O(1)–Zn(1), 2.048 Å; O(2)–Zn(2), 2.041 Å) in the same tendency as **2a** (Table 6). Each side of the two planes of a central Zn₂O₂ four-membered ring was covered with one pyrrolidine ring that concealed the active zinc centers, which would result in the decrease of catalytic activity.

Conclusions

We have reported the asymmetric alternating copolymerization of cyclohexene oxide and CO₂ with chiral dimeric zinc complexes. The isolated zinc complex **2a**, prepared by the reaction of Et₂Zn with (*S*)-diphenyl(pyrrolidin-2-yl)methanol (**1a-H**), was characterized by X-ray single-crystal diffraction. The zinc centers, each of which is coordinated by two bridging oxygens, one nitrogen in a pyrrolidine ring, and one ethyl group, possess distorted tetrahedral geometries and two ethyl groups oriented in syn fashion. The dimeric zinc complex **2a** was found to be effective for the asymmetric alternating copolymerization of cyclohexene oxide and CO₂ to give optically active poly-

carbonate at 49% ee. The MALDI-TOF mass spectrum of the copolymer proved that the chiral ligand **1a** worked as an initiator and that the copolymerization was initiated by the insertion of CO₂ into a Zn–O bond of **2a**. Addition of ethanol to **2a** gave dimeric zinc complex **3a-OEt** with which the catalytic activities and enantioselectivities were improved up to 95% yield and 80% ee, respectively. From these results, we indicated a possibility of the reaction mechanism in which dimeric zinc species took part in the copolymerization, and a high degree of chiral recognition was achieved by the aggregated zinc complex bearing two chiral ligands. Various prolinol derivatives with a substituent on the phenyl group of **1a-H** was also investigated and shown to have a great effect on catalytic activity and stereoselectivity, suggesting that further optimization of the ligand would lead to an achievement of the improved catalyst.

Experimental Section

General Methods. All manipulations involving air- and/or moisture-sensitive compounds were carried out using the standard Schlenk technique under argon purified by passing it through a hot column packed with BASF catalyst R3-11. NMR spectra were recorded in deuteriochloroform on a Varian Mercury 200 (¹H 200 MHz; ¹³C 50 MHz) or JEOL JNM-ECP500 (¹H 500 MHz; ¹³C 125 MHz) spectrometer. Chemical shifts are reported in ppm from an internal standard: tetramethylsilane (0 ppm) for ¹H and deuteriochloroform (77.0 ppm) for ¹³C. Melting points were determined on a Yanaco MP-500D melting point apparatus. Optical rotation was measured on a JASCO DIP-360 spectrometer using a 1-dm cell. IR spectra were recorded on a JASCO IR-810 spectrometer or a SHIMADZU FTIR-8100A spectrometer. Gel permeation chromatography (GPC) analyses were carried out using a GL Sciences instrument (HPLC pump PU610, LC column oven MODEL556) equipped with a Shodex SE-61 RI detector, SIC GPC board, and two columns (Shodex KF-804L). The GPC columns were eluted with tetrahydrofuran at 40 °C at 1 mL/min. Gas chromatography was performed on a SHIMADZU GC-14B with a J&W Scientific DB-1 column and helium as the carrier gas. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30. Heating rates were 10 °C/min. The reported *T*_g value was determined from the second heating scan. Elemental analyses were performed at the Microanalysis Center, Kyoto University.

All the solvents and cyclohexene oxide used for reactions were distilled under argon after drying over an appropriate drying reagent. Most of the reagents were purchased from Aldrich Chemical Co. or Wako Pure Chemical Industries Ltd and were used without further purification unless otherwise specified. Carbon dioxide (Teisan Co., 99.8%) was used as received. For silica gel column chromatography, Wako-gel C-200 was used.

Ligand Synthesis

Synthesis of *N*-Benzyl-(*S*)-diphenyl(pyrrolidin-2-yl)methanol (4a**).** A flame-dried 200-mL two-necked flask fitted with an argon inlet and a 50-mL addition funnel containing bromobenzene (6.2 mL, 59 mmol) in THF (35 mL) was charged with magnesium turnings (1.5 g, 62 mmol) and THF (15 mL). A small portion (2 mL) of a solution of bromobenzene in THF was added with stirring at room temperature. After the exothermic reaction started, the reaction flask was cooled at 10 °C with a water bath. The remaining bromobenzene was added with stirring over 30 min, and then the reaction mixture was stirred at room temperature for 3 h. A solution of *N*-benzyl-(*S*)-proline methyl ester (5.2 g, 24 mmol) in THF (10 mL) was placed in the addition funnel and added slowly with stirring at 10 °C. After the addition, the reaction mixture was stirred at room temperature for 20 h, and then acidified with 3 M aqueous HCl (50 mL). The whole mixture was concentrated by evaporation to remove most of the amount of THF, and ether (100

mL) was added to the resulting mixture. Vigorous stirring of the biphasic solution gave a pale yellow precipitation of *N*-benzyl-(*S*)-diphenyl(pyrrolidin-2-yl)methanol hydrochloride, which was collected by filtration. To liberate the free base, the salt was suspended in ether (300 mL) and 1 M aqueous NaOH (100 mL), and then the resulting mixture was stirred vigorously until the salt was completely dissolved. After the organic layer was separated, the aqueous layer was extracted with ether (100 mL × 2). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give almost pure **4a**, which was used for the next reaction without further purification.

Synthesis of (*S*)-Diphenyl(pyrrolidin-2-yl)methanol (1a-H**).** In a 250-mL Schlenk tube were placed **4a** (7.3 g, 21 mmol), palladium hydroxide on carbon (20 wt %, 900 mg), acetic acid (1.3 mL, 23 mmol), dichloromethane (20 mL), and methanol (40 mL). The mixture was stirred under a hydrogen atmosphere (1 atm) at room temperature for 47 h, filtered, and concentrated in vacuo. To liberate the free base, the salt was suspended in ether (300 mL) and 1 M aqueous NaOH (100 mL), and then the resulting mixture was stirred vigorously until the salt was completely dissolved. The organic layer was separated, and the aqueous layer was extracted with ether (100 mL × 2). The combined organic extracts were washed with brine (100 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography with ethyl acetate as an eluent gave **1a-H** (4.9 g, 92% yield) as a colorless solid. [α]²²_D –60.0° (c 0.95, MeOH) [lit.³⁴ [α]²¹_D –54.3° (c 0.261, MeOH)]; ¹H and ¹³C NMR data were identical with literature.³⁴

Synthesis of *N*-Benzyl-(*S*)-bis(3-methoxyphenyl)(pyrrolidin-2-yl)-methanol (4b**).** A crude sample was prepared from 3-bromo-1-methylbenzene (3.0 mL, 25 mmol) and *N*-benzyl-(*S*)-proline methyl ester (2.2 g, 10 mmol) according to the procedure described previously. Purification by silica gel column chromatography with hexanes–ethyl acetate (10:1, *R*_f 0.26) as an eluent gave **4b** (3.5 g, 94% yield) as a white solid, mp 86–88 °C. [α]²²_D 95.5° (c 0.43, CHCl₃); ¹H NMR (CDCl₃) δ 7.54 (s, 1H), 7.46 (d, 1H, *J* = 7.8 Hz), 7.40 (s, 1H), 7.35 (d, 1H, *J* = 7.8 Hz), 7.25–7.12 (m, 5H), 7.04 (d, 2H, *J* = 6.9 Hz), 6.97 (d, 1H, *J* = 7.8 Hz), 6.89 (d, 1H, *J* = 7.8 Hz), 4.86 (brs, 1H), 3.92 (dd, 1H, *J* = 9.6, 4.6 Hz), 3.17 (d, 1H, *J* = 12.8 Hz), 3.01 (d, 1H, *J* = 12.8 Hz), 2.91 (m, 1H), 2.37–2.26 (m, 7H), 2.01–1.92 (m, 1H), 1.80–1.72 (m, 1H), 1.69–1.55 (m, 2H); ¹³C NMR (CDCl₃) δ 147.90, 146.48, 139.80, 137.61, 137.58, 128.57, 128.05, 127.96, 127.78, 127.05, 126.96, 126.76, 126.38, 126.22, 122.83, 122.56, 77.96, 70.72, 60.57, 55.60, 29.82, 24.22, 21.71, 21.66. Anal. Calcd for C₂₆H₂₉NO: C, 84.06; H, 7.87. Found: C, 84.02; H, 7.92.

Synthesis of (*S*)-Bis(3-methoxyphenyl)(pyrrolidin-2-yl)methanol (1b-H**).** This compound was prepared from **4b** (3.3 g, 8.9 mmol) according to the procedure described for **1a-H**. Purification by silica gel column chromatography with ethyl acetate (*R*_f 0.18) as an eluent gave **1b-H** (2.5 g, 99% yield) as a colorless viscous oil. [α]²²_D –63.0° (c 0.28, CHCl₃); ¹H NMR (CDCl₃) δ 7.38 (s, 1H), 7.36–7.32 (m, 2H), 7.26 (d, 1H, *J* = 7.8 Hz), 7.19–7.13 (m, 2H), 6.96 (d, 2H, *J* = 7.3 Hz) 4.22 (t, 1H, *J* = 7.6 Hz), 3.03–2.98 (m, 1H), 2.95–2.88 (m, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 1.77–1.52 (m, 4H); ¹³C NMR (CDCl₃) δ 148.13, 145.31, 137.72, 137.44, 127.14, 127.03, 126.62, 126.13, 122.49, 64.47, 46.70, 26.22, 25.48, 21.66, 21.65. Anal. Calcd for C₁₉H₂₃NO: C, 81.10; H, 8.24. Found: C, 81.07; H, 8.36.

Synthesis of *N*-Benzyl-(*S*)-bis(3-methoxyphenyl)(pyrrolidin-2-yl)-methanol (4c**).** The reaction was carried out with 3-bromo-1-methoxybenzene (2.2 mL, 18 mmol) and *N*-benzyl-(*S*)-proline methyl ester (1.5 g, 7.0 mmol) according to the procedure described previously. Acidification with 3 M aqueous HCl and removal of most of the amount of THF gave a pale yellow oil. After the acidic aqueous layer was removed by decantation, the remaining oil was completely dissolved in ether (200 mL) and 1 M aqueous NaOH (100 mL) to give free base. After the organic layer was separated, the aqueous layer was extracted with ether (100 mL × 2). The combined organic layers were washed

with brine (100 mL), dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography with hexanes–ethyl acetate (3:1, R_f 0.45) gave **4c** (2.30 g, 81% yield) as a colorless viscous oil. $[\alpha]_D^{25}$ 68.4° (c 0.60, CHCl_3); ^1H NMR (CDCl_3) δ 7.34–7.13 (m, 9H), 7.06 (d, 2H, J = 6.9 Hz), 6.70 (dd, 1H, J = 7.8, 2.3 Hz), 6.63 (dd, 1H, J = 8.3, 2.3 Hz), 4.97 (brs, 1H), 3.92 (dd, 1H, J = 9.2, 4.6 Hz), 3.79 (s, 3H), 3.75 (s, 3H), 3.28 (d, 1H, J = 12.8 Hz), 3.05 (d, 1H, J = 12.8 Hz), 2.94–2.89 (m, 1H), 2.39–2.31 (m, 1H), 2.01–1.91 (m, 1H), 1.79–1.71 (m, 1H), 1.68–1.55 (m, 2H); ^{13}C NMR (CDCl_3) δ 159.47, 159.31, 149.75, 148.14, 139.73, 128.94, 128.55, 128.09, 118.18, 111.75, 111.72, 111.43, 111.38, 77.76, 70.54, 60.44, 55.52, 55.12, 29.78, 24.08. Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3$: C, 77.39; H, 7.24. Found: C, 77.28; H, 7.24.

Synthesis of (S)-Bis(3-methoxyphenyl)(pyrrolidin-2-yl)methanol (1c-H). A crude material was prepared from **4c** (2.1 g, 5.3 mmol) according to the procedure described for **1a-H**. Purification of the crude product by silica gel column chromatography with ethyl acetate (R_f 0.12) as an eluent gave **1c-H** (1.6 g, 97% yield) as a colorless viscous oil. $[\alpha]_D^{25}$ –62.4° (c 0.83, CHCl_3); ^1H NMR (CDCl_3) δ 7.25–7.11 (m, 6H), 6.72–6.68 (m, 2H), 4.19 (t, 1H, J = 7.6 Hz), 3.77, (s, 3H), 3.76 (s, 3H), 3.03–2.98 (m, 1H), 2.94–2.88 (m, 1H), 1.77–1.52 (m, 4H); ^{13}C NMR (CDCl_3) δ 159.50, 159.27, 149.81, 146.85, 129.09, 128.83, 118.02, 117.88, 112.07, 111.48, 111.45, 76.93, 64.42, 55.08, 46.66, 26.17, 25.40. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$: C, 72.82; H, 7.40. Found: C, 72.86; H, 7.52.

Synthesis of N-Benzyl-(S)-bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol (4d). This was prepared from 1-bromo-3,5-dimethylbenzene (3.1 mL, 23 mmol) and *N*-benzyl-(*S*)-proline ethyl ester (2.1 g, 9.0 mmol) according to the procedure described previously and purified by silica gel column chromatography with hexanes–ethyl acetate (10:1, R_f 0.44) as an eluent to give **4d** (3.3 g, 92% yield) as a colorless viscous oil. $[\alpha]_D^{25}$ 106° (c 1.20, CHCl_3); ^1H NMR (CDCl_3) δ 7.28 (s, 2H), 7.26–7.16 (m, 5H), 7.06–7.03 (m, 2H), 6.80 (s, 1H), 6.70 (s, 1H), 4.77 (brs, 1H), 3.88 (dd, 1H, J = 9.6, 4.1 Hz), 3.14 (d, 1H, J = 12.8 Hz), 3.00 (d, 1H, J = 12.8 Hz), 2.93–2.88 (m, 1H), 2.37–2.30 (m, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 2.01–1.91 (m, 1H), 1.80–1.72 (m, 1H), 1.68–1.52 (m, 2H); ^{13}C NMR (CDCl_3) 147.85, 146.40, 139.95, 137.32, 137.27, 128.63, 128.03, 127.98, 127.88, 126.73, 123.48, 123.45, 77.99, 70.78, 60.59, 55.67, 29.87, 24.29, 21.63, 21.55. Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{NO}$: C, 84.17; H, 8.32. Found: C, 84.27; H, 8.39.

Synthesis of (S)-Bis(3,5-dimethylphenyl)(pyrrolidin-2-yl)methanol (1d-H). This material was prepared from **4d** (3.1 g, 7.7 mmol) according to the procedure described for **1a-H** and purified by silica gel column chromatography with hexanes–ethyl acetate (1:2, R_f 0.11) as an eluent to give **1d-H** (2.2 g, 92% yield) as a colorless solid. ^1H and ^{13}C NMR data were identical with literature.³⁴

Synthesis of N-Benzyl-(S)-bis[4-(trifluoromethyl)phenyl](pyrrolidin-2-yl)methanol (4e). This material was prepared from 1-bromo-4-trifluoromethylbenzene (2.5 mL, 17.5 mmol) and *N*-benzyl-(*S*)-proline ethyl ester (1.63 g, 7.0 mmol) according to the procedure described previously and purified by silica gel column chromatography with hexanes–ethyl acetate (10:1, R_f 0.48) as an eluent to give **4e** (3.0 g, 91% yield) as a colorless viscous oil. $[\alpha]_D^{25}$ 49.8° (c 2.0, CHCl_3); ^1H NMR (CDCl_3) δ 7.86 (d, 2H, J = 8.3 Hz), 7.70 (d, 2H, J = 8.3 Hz), 7.58–7.52 (m, 4H), 7.27–7.18 (m, 3H), 7.03–6.99 (m, 2H), 5.23 (brs, 1H), 4.04 (dd, 1H, J = 9.2, 4.1 Hz), 3.26 (d, 1H, J = 12.8 Hz), 3.11 (d, 1H, J = 12.8 Hz), 2.98–2.93 (m, 1H), 2.41–2.39 (m, 1H), 2.01–1.90 (m, 1H), 1.69–1.61 (m, 2H); ^{13}C NMR (CDCl_3) δ 151.46, 149.84, 138.96, 129.05 (q, 32 Hz), 128.83 (q, 32 Hz), 128.36, 128.30, 127.12, 125.97, 125.80, 125.38 (q, 3.8 Hz), 125.25 (q, 3.8 Hz), 124.07 (q, 272 Hz), 123.99 (q, 272 Hz), 77.55, 70.35, 60.40, 55.45, 29.82, 23.92. Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{NOF}_6$: C, 65.13; H, 4.84. Found: C, 65.08; H, 4.85.

Synthesis of (S)-Bis[4-(trifluoromethyl)phenyl](pyrrolidin-2-yl)methanol (1e-H). This amino alcohol was prepared from **4e** (3.9 g, 8.2 mmol) according to the procedure described previously and purified of the crude product by silica gel column chromatography with ethyl

acetate as an eluent to give **1e-H** (2.9 g, 91% yield) as a colorless solid. $[\alpha]_D^{25}$ –38.7° (c 1.7, MeOH) [lit.³⁴ $[\alpha]_D^{25}$ –34.2° (c 0.789, MeOH)]; ^1H and ^{13}C NMR data were identical with literature.³⁴

Synthesis of Complex 2a from Et₂Zn and 1a-H. In a flame-dried 80-mL Schlenk tube was placed (*S*)-diphenyl(pyrrolidin-2-yl)methanol **1a-H** (0.53 g, 2.1 mmol) and THF (20 mL). To the solution was added Et_2Zn (1.05 M in hexane, 2.0 mL, 2.1 mmol) with stirring at room temperature. After ethane gas evolution ceased, the resulting mixture was stirred at 60 °C for 2 h and then concentrated and dried in vacuo. The resulting white solid was recrystallized from THF/hexane at –20 °C to give colorless crystals (350 mg, 51% yield).

Synthesis of Complex 2e from Et₂Zn and 1e-H. In a flame-dried 80-mL Schlenk tube was placed **1e-H** (0.78 g, 2.0 mmol) and toluene (10 mL). To the solution was added Et_2Zn (1.05 M in hexane, 1.9 mL, 2.0 mmol) with stirring at room temperature. After ethane gas evolution ceased, the resulting mixture was stirred at 60 °C for 2 h and then concentrated in vacuo. The resulting white solid was recrystallized from toluene/hexane at –20 °C to give colorless crystals (521 mg, 49% yield).

X-ray Crystallography. Suitable single crystals were selected under ambient conditions, attached to the tip of a glass fiber and then mounted in a Bruker SMART system at 130 K. The X-ray data were collected on a Bruker SMART CCD diffractometer and were covered more than a hemisphere of reciprocal space by three sets of frames. Each of the frame sets had a different φ , and each of the frames were collected with 0.30° steps in ω .

Space groups were determined on the basis of systematic absences and intensity statistics. The crystal structures were solved by direct method and refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in ideal positions with isotropic thermal parameters. Crystallographic data for **2a** and **2e** are summarized in Table 7.

Copolymerization of Cyclohexene Oxide and CO₂ with Dimeric Zinc Complex 2a. A flame-dried 80-mL Schlenk tube was charged with zinc complex **2a** (170 mg, 0.25 mmol) and toluene (17 mL). After complex **2a** was allowed to dissolve completely by stirring at 60 °C, the resulting homogeneous solution was cooled to room temperature and transferred into a 50-mL autoclave followed by introduction of cyclohexene oxide (1.0 mL, 10 mmol) and carbon dioxide (30 atm). After stirring at 40 °C for 19 h, the reaction mixture was cooled to ambient temperature and the CO₂ pressure was slowly released. The mixture was diluted with toluene (30 mL) and washed with aq HCl (1M, 10 mL × 2) and brine (10 mL × 2). The organic layer was dried over Na_2SO_4 and concentrated to 5 mL by evaporation. The copolymer was precipitated by adding MeOH (100 mL), filtered through a pad of Celite, washed with MeOH, and eluted by CH_2Cl_2 . The eluent was concentrated by evaporation and dried in vacuo to give the copolymer.

MALDI-TOF Mass Spectroscopy. MALDI-TOF mass spectrometric measurements were performed on a PerSeptive Biosystems Voyager DE-STR equipped with a 337-nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. An accelerating voltage of 20 kV was used, and all mass spectra were recorded in the linear mode. In general, mass spectra from 256 laser shots were accumulated to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (BACHEM) and insulin (bovine pancreas 28.3; MW = 5733.50) (Nacalai) were used as internal standards to calibrate the mass scale.

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 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.

Representative Procedure for Copolymerization of Cyclohexene Oxide and CO₂ with In Situ Generated 3a-OR. To the homogeneous toluene (17 mL) solution of zinc complex **2a** (170 mg, 0.25 mmol), prepared in the same manner as mentioned previously, in a 50-mL

Table 7. Crystallographic Data for Complexes **2a** and **2e**

compound	2a	2e
empirical formula	C ₃₈ H ₄₆ N ₂ O ₂ Zn ₂	C ₄₉ H ₅₀ F ₁₂ N ₂ O ₂ Zn ₂
FW	693.51	1057.65
crystal system	monoclinic	orthorhombic
space group	<i>P</i> 2(1)	<i>P</i> 2(1)2(1)2(1)
color of crystal	colorless	colorless
unit cell dimensions		
<i>a</i> , Å	9.3266(5)	14.5089(16)
<i>b</i> , Å	15.8144(8)	14.6962(16)
<i>c</i> , Å	11.1575(6)	22.214(3)
α, deg	90	90
β, deg	90.1950(10)	90
γ, deg	90	90
<i>V</i> , Å ³	1645.66(15)	4736.6(9)
<i>Z</i>	2	4
<i>T</i> , K	130(2)	130(2)
<i>d</i> _{calcd.} , g/cm ³	1.400	1.483
absorption coefficient, nm ⁻¹	1.494	1.101
reflections collected	13569	37630
independent reflections	8977 [<i>R</i> (int) = 0.0176]	13358 [<i>R</i> (int) = 0.0988]
max. and min. transmission	0.7544 and 0.6628	0.7336 and 0.6672
goodness-of-fit on <i>F</i> ²	0.977	0.632
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0310, <i>wR</i> 2 = 0.0703	<i>R</i> 1 = 0.0480, <i>wR</i> 2 = 0.0898
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0341, <i>wR</i> 2 = 0.0711	<i>R</i> 1 = 0.1398, <i>wR</i> 2 = 0.1196

autoclave were added a specified amount of alcohol (0.20 M in toluene), cyclohexene oxide (1.0 mL, 10 mmol), and CO₂ (30 atm). After stirring at 40 °C for 19 h, the reaction mixture was cooled to ambient temperature and the CO₂ pressure was slowly released. The workup procedure as described in the copolymerization with **2a** gave the copolymer.

Copolymerization of Cyclohexene Oxide and CO₂ as a Function of Conversion. All copolymerization reactions were carried out with **3a-OEt** which was generated in situ by the reaction of **2a** and 0.8 equiv of ethanol. After an appropriate reaction time, decane was added as internal standard for GC analysis. An aliquot (~0.2 mL) of the resulting mixture was withdrawn, quenched with methanol, and analyzed by GC. The rest of the reaction mixture was worked up in the same manner as previously mentioned to give the copolymer.

Preparation of 3a-OEt. In a flame-dried 80-mL Schlenk tube was placed **1a-H** (0.51 g, 2.0 mmol) and THF (18 mL). To the solution was added Et₂Zn (1.10 M in hexane, 1.8 mL, 2.0 mmol) with stirring at room temperature. After ethane gas evolution was ceased, the resulting mixture was stirred at 60 °C for 2 h and then cooled to room temperature. Following the addition of ethanol (51 μL, 0.90 mmol) in toluene (1.0 mL), the mixture was stirred at room temperature for 1 h

and then concentrated in vacuo. The resulting white solid was recrystallized from THF/hexane at -20 °C to give colorless crystals.

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Supporting Information Available: Crystallographic information files (CIF) for **2a** and **2e**. MALDI-TOF mass spectra of the copolymers with a mixture of **2a** and various alcohols, ROH (R = Me, Bn, ^{*i*}Pr, ^{*t*}Bu, CF₃CH₂) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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