Copolymers

Highly Enantioselective Catalytic System for Asymmetric Copolymerization of Carbon Dioxide and Cyclohexene Oxide

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Abstract: A new ligand can be easily prepared, and its intramolecular dinuclear zinc complexes act as a high performance catalyst for the asymmetric alternating copolymerization of cyclohexene oxide and CO_2 under very mild conditions (1 atm CO_2 , room temperature), affording completely alternating polycarbonates with up to 93.8% enantiomeric excess (*ee*) and 98% yield. A high M_n value of 28600 and a relatively narrow polydispersity (M_w/M_n ratio) of 1.43 were also achieved.

Optically active polymers are considered as candidates for new and valuable materials because of the well-defined chemical structures and special physical properties of these polymers.^[1] Catalytic asymmetric polymerization is an efficient method to prepare chiral polymers from achiral monomers because a small amount of chiral catalyst repeatedly activates prochiral molecules, controlling the stereochemistry to yield a large amount of chiral polymer. Recently, asymmetric copolymerization of cyclohexene oxide (CHO) and CO_{2} affording chiral polycarbonates, has attracted much attention for several reasons: 1) CO₂ is a relatively nontoxic, naturally abundant onecarbon chemical feedstock, and is also the major greenhouse gas; 2) meso-epoxides, such as CHO are an ideal substrate for desymmetrization using chiral catalysts;^[3] 3) the resulting chiral polycarbonates not only have a relatively high glass-transition temperature and tensile strength, but are also degradable,^[4] giving optically active cyclohexane-1,2-diol.

Since the initial report by Inoue et al. on the copolymerization of CO₂ with epoxides in 1969,^[5] this type of copolymerization reaction has been studied extensively, and great progress has been made.^[6] However, very few examples of the asymmetric copolymerization of CO₂ and CHO have been reported.^[2] In 1999, Nozaki et al.^[2a] described the first asymmetric copolymerization of CHO and CO₂ with moderate enantioselectiv-

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1

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ity (73% *ee*) by using a catalytic amount of chiral catalyst **1** (Figure 1) at 40 °C and 30 atm CO₂. In the presence of additional ethanol, the enantioselectivity increased up to 80% *ee*.^[2c] Subsequently, Coates et al. developed chiral zinc oxazoline catalyst **2** (Figure 1), which demonstrated similar enantioselectivity (72% *ee*) at 20 °C and 6.8 atm CO₂, for this copolymerization.^[2b] Lu et al. reported chiral (*R*,*R*)-salen cobalt(III) complex **3a** (Figure 1) for the asymmetric copolymerization of CHO with CO₂ in the presence of quaternary ammonium salt co-catalysts.^[2g,h] This method exhibited lower enantioselectivity



Figure 1. The structures of chiral catalysts 1–6.

(up to 38% *ee*) at 25 °C and 6 atm CO₂.^[2h] A moderate to good enantioselectivity (60–80% *ee*) was also observed in the copolymerization of CO₂ and CHO catalyzed by optically active dinuclear aluminum complexes **5**, in conjunction with a bulky Lewis base as catalyst activator.^[2j] General drawbacks of currently existing methods include: 1) Relatively low enantioselectivity, which is in great contrast to the highly enantioselective desymmetrization of *meso*-epoxides (>90% *ee*) with chiral catalysts;^[7] 2) substantial pressures of CO₂, significantly increasing the overall energy requirement of the process.



Recently, Lu et al. have made great progress in the highly enantioselective copolymerization of CO₂ with CHO.^[8] They reported a highly enantioselective catalyst system for this asymmetric copolymerization by using the dissymmetric chiral (S,S)salen cobalt(III) complex 3b, bearing an adamantyl group on the phenolate ortho position.^[8a] It was found that the presence of stoichiometric quantities of a chiral induction agent (3 equivalents), such as (S)-propylene oxide or (S)-2-methyltetrahydrofuran, could significantly improve the enantioselectivity. In the presence of (S)-2-methyltetrahydrofuran (3 equivalents), at -25 °C and 8 atm CO₂, up to 96% ee was achieved in the resultant polycarbonates, although this asymmetric alternating copolymerization showed low conversions (45%) and lower M_n values (less than 10000 g mol⁻¹). A high enantioselectivity of up to 98% ee was also observed by the same group in the presence of dinuclear cobalt(III) complexes (S,S,S,S)-6 at $0\,^{\circ}\text{C}$ and 20 atm CO_2. $^{[8b]}$

Therefore, it is highly desirable that a new catalytic system, using only a catalytic amount of chiral ligand and no additional chiral induction agent, is developed for the copolymerization of CO₂ and CHO, resulting in a high M_n value (> 20000 g mol⁻¹) and providing high catalytic performance, enantioselectivity, and chemical yield under mild conditions. Meeting these goals is challenging, and focuses mainly on catalyst design.

Based on the mechanistic understanding that a dimeric zinc complex was involved in the transition state of the epoxide ring-opening event during CO₂/CHO copolymerization, Ding et al. developed a chiral dinuclear metal catalyst **4**,^[2d,f] which was coordinated with Trost's multidentate ligand. This catalyst exhibited moderate activity and very low enantioselectivity (8–18% *ee*) for copolymerization of CHO and CO₂, but most inter-

estingly, the catalyst was more active under only one atm CO_2 pressure. We believe that the main reason for the low *ee* value could be the mismatch of chiral microenvironment. The development of new chiral ligands plays a key role for overcoming this limitation because subtle changes in conformational, steric, and/or electronic properties of the ligands can often result in dramatic variation of the enantioselectivity.

In recent years, we have explored the use of chiral small-ring heterocycle ligands in catalytic asymmetric synthesis.^[9] We have found that among these chiral nitrogen heterocycles containing a β -amino alcohol moiety, the use of four-membered heterocycles as chiral ligands affords the best enantioselectivity in the catalytic asymmetric addition of diethylzinc to benzaldehyde. This activity is owing to the relatively rigid ligand skeleton and appropriate chiral microenvironment provided by the four-membered heterocycle.^[9a] Herein, we report the synthesis of new chiral ligand 9 with a more rigid azetidine ring compared with that of pyrrolidine (Scheme 1), and its application in the asymmetric copolymerization of CHO and CO₂ with excellent enantioselectivity of up to 93.8% ee.



Scheme 1. Synthesis of the chiral ligand 9.

The chiral ligand 9 was easily prepared from azetidin-2-yl-(diphenyl)-methanol 7 and 2,6-bis(bromomethyl)-p-cresol 8, according to a procedure by Trost et al.^[10] Initially, we conducted the copolymerization of CO₂ and CHO under the conditions reported by Ding et al.^[2d] The copolymerization reaction was carried out at one atm of CO₂, in toluene at 60 °C, for 36 h in the presence of 5 mol% of the ligand 9, 10 mol% ZnEt₂, and 2 mol% EtOH. Gratifyingly, the chiral compound 9 showed similar activity to that of the ligand by Trost et al., giving poly(cyclohexene carbonate, PCHC) **10** in a quantitative yield (>99%) and with a relatively high M_n value of 17000 g mol⁻¹ and a relatively narrow polydispersity (M_w/M_n ratio) of 1.21 (Table 1, entry 1). The enantioselectivity of the copolymerization reaction was also determined by a procedure described by Nozaki et al.^[2a] The treatment of PCHC 10 with aqueous NaOH afforded cyclohexane-1,2-diol 11 in 85% yield, followed by the transformation of 11 into dibenzoate 12. The ee value of dibenzoate 12 was determined by HPLC analysis with a chiral column (Sino-Chiral AS). To our delight, the enantioselectivity of the resulting dibenzoate 12 was up to 86.7% ee with (S,S)-configuration (Table 1, entry 1).

Table 1. Asymmetric alternating copolymerization of CO_2 and $\text{CHO}^{[a]}$												
$ \begin{array}{c} O \\ + CO_2 \\ EIOH \\ EIOH \\ \end{array} \begin{array}{c} O \\ ZnEt_2 \\ EIOH \\ \end{array} \begin{array}{c} O \\ O \\ THF/CH_3OH \\ O \\ n \\ \end{array} \begin{array}{c} NaOH/H_2O \\ THF/CH_3OH \\ HO \\ OH \\ Et_3N \\ PhCOC \\ OH \\ Et_3N \\ OH \\ U \\ 12 \\ 0 \\ \end{array} \begin{array}{c} PhCOC \\ DMAP \\ OH \\ Et_3N \\ OH \\ U \\ $												
Entry	Solvent	T [°C]	t [h]	Yield of [%] ^[b]	10	<i>M</i> _n of 10 ^[c]	PDI ^[c]	Yield of 11 [%] ^[b]	Yield of 12 [%] ^[b]	ee of 12 [%] ^[d]		
1	PhCH₃	60	36	>99		17000	1.21	85	83	86.7		
2	hexane	60	36	66		12900	1.12	79	97	63.7		
3	CCl ₄	60	36	80		13300	1.17	83	93	74.3		
4	benzene	60	36	73		18700	1.33	97	80	48.8		
5	DCE	60	36	40		9550	1.08	87	77	85.6		
6	PhCH₃	60	24	87		12500	1.17	96	79	68.6		
7	PhCH₃	60	12	87		11 300	1.17	96	83	75.3		
8	PhCH₃	60	6	83		11 200	1.18	87	90	80.2		
9	PhCH₃	60	48	>99		13100	1.19	80	97	71.0		
10	PhCH₃	80	36	79		11 200	1.21	89	98	69.6		
11	PhCH₃	40	36	96		28200	1.33	97	93	89.4		
12	PhCH₃	30	36	99		26000	1.46	90	99	90.9		
13	PhCH₃	20	36	98		28600	1.43	97	96	93.8		
14	$PhCH_3$	10	36	99		29800	1.15	91	99	93.3		
[a] All reactions performed by using 5 mol% ligand 9, 10 mol% ZnEt ₂ , and 2 mol% EtOH, 1 atm CO ₂ pressure. [b] Yield of isolated product. [c] Estimated by gel-permea-												

EtOH, 1 atm CO_2 pressure. [b] Yield of isolated product. [c] Estimated by gel-permeation chromatography using a polystyrene standard. [d] Determined by HPLC analysis with a chiral column (Sino-Chiral AS). The product chromatograms were compared against a known racemic mixture.

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To explore the effect of solvents on the efficiency and enantioselectivity of the copolymerization reaction, we varied the solvent from toluene to hexane, CCl_4 , benzene, or 1,2-dichlorethane (DCE) (Table 1, entries 2–5), among which toluene was found to be the best solvent with respect to both yield and enantioselectivity. DCE afforded high *ee* values (85.6%), but the yield of copolymerization was very low (40%).

The effect of reaction time on the efficiency and enantioselectivity of the copolymerization reaction was also examined (Table 1, entries 1 and 6–9). Reducing the reaction time from 36 to 24, 12, and 6 h led to a decrease in the reaction yield and the M_n value. These results suggested that a chain-transfer reaction existed. However, the enantioselectivity showed no obvious regular change with the variation of reaction time.

Temperature proved to have a distinctive effect on the *ee* value. An increase in temperature from 60 to 80 °C resulted in a decrease in enantioselectivity from 86.7 to 69.6% *ee* (Table 1, entries 10 and 1), whereas decreasing the reaction temperature from 60 to 40 °C led to an enhancement in enantioselectivity from 86.7 to 89.4% *ee* (Table 1, entries 11 and 1). Lowering the temperature to 20 °C resulted in an *ee* value of up to 93.8% (Table 1, entry 13). On decreasing the reaction temperature to 10 °C, the alternating copolymerization showed almost the same enantioselectivity as that at 20 °C (93.3% *ee* and 93.8% *ee*, respectively).

Because the resultant chiral poly(cyclohexene) carbonate was easily hydrolyzed to *trans*-cyclohexane-1,2-diol by using aqueous NaOH, this highly enantioselective copolymerization reaction of CHO and CO_2 offers a promising alternative strategy for the synthesis of chiral cyclohexane-1,2-diol.^[5,11]

To demonstrate that the zinc complex involved an intramolecular dinuclear structure, which is critical for two proximal zinc species to activate the substrates cooperatively during the catalysis, the zinc complex was prepared by reacting **9** with diethylzinc in toluene, followed by benzoic acid (Scheme 2). The resulting solution was left to stand for several days in order to obtain a single crystal of the dinuclear zinc complex **14**. Although numerous attempts to isolate **14** proved to be unsuccessful, a pale yellow solid was afforded after slow evaporation of solvent. The direct determination of the identity of this solid by using electrospray mass spectrometry showed that a series of peaks between m/z 857–865 were consistent with the formula $C_{48}H_{44}N_2O_5Zn_2$, corresponding to the $[M+H]^+$ peak of **14**, containing a benzoic acid anion, whereas a series of peaks between m/z 979–987 were in accordance with the formula $C_{55}H_{50}N_2O_7Zn_2$, corresponding to the $[M+H]^+$ peak of **15**, containing a benzoic acid anion and a benzoic acid molecule. ESI-MS studies indicated that the zinc complex involved an intramolecular dinuclear structure. Although the precise structures of the dinuclear zinc complexes **14** are currently not known, we favor the carboxylate-bridged dinuclear zinc structure, as depicted in **14**, because some related carboxylate-bridged dinuclear zinc complexes have already been determined^[12] or proposed.^[2d, 13]

Compared with the pyrrolidine-based ligand of the same type, azetidine-based ligand **9** showed a substantial improvement in enantioselectivity. The only difference between these ligands is the ring size of the pyrrolidine and azetidine. Ligand **9** possesses a more rigid-ring backbone and is more sterically congested than five-membered heterocycle-based ligands. Therefore, the intramolecular dinuclear zinc structure of the catalytically active species containing an azetidine ring is more rigid than that containing a pyrrolidine ring. This rigidity is responsible for the large improvement in enantioselectivity.

To obtain more information about the active species and the origins of enantioselectivity, theoretical calculations were carried out to study the intramolecular $S_N 2$ attack of the carbonate ester at the back side of the *cis*-epoxide.^[14] This step is the stereoselectivity-determining and rate-determining step according to the reports of Rieger et al.^[15] and Williams et al.^[16] We optimized the transition states and calculated the free energies of the $S_N 2$ reaction step in toluene at the ω B97XD/6-31G(d)^[17] level by using the conductor-like polarizable continuum model (CPCM) method,^[18] which was successfully applied by Williams et al.^[16] on the study of similar reaction mechanisms. Figure 2 illustrates the optimized structures of the two key transition states (TS), that is, TS-*re* (associated with the



Scheme 2. The possible structures of intramolecular dinuclear zinc complexes.

 $\begin{bmatrix} EtO & O & Ph \\ Ph & O & O & Ph \\ Ph & Zn & Zn & Ph \\ N & O & N & Ph \\ TS-re & Me \end{bmatrix}^{\dagger} \begin{bmatrix} EtO & O & Ph \\ Ph & O & O & Ph \\ Ph & Zn & Zn & Ph \\ Me & TS-si \end{bmatrix}^{\dagger}$

Figure 2. The structures of intramolecular $S_N 2$ transition states optimized at the ω B97XD/6-31G(d) level.

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Chem. Eur. J. 2014, 20, 1–6 www.chemeurj.org These are not the final page numbers! 77 (*R*,*R*)-product) and TS-*si* (associated to the (*S*,*S*)-product). All calculations were carried out with Gaussian 09 programs.^[19]

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The calculated results shows that TS-*si*, which formed the experimentally observed major (*S*,*S*)-product, was favored, by 1.9 kcal mol⁻¹, compared to TS-*re* (Figure 2). This energy value is in agreement with an *ee* value of approximately 92.2% (see the Supporting Information), which is very close to the value obtained experimentally (93.8%, Table 1, entry 13).

Based on the model of the transition state for the azetidinebased catalyst system, the prediction of the pyrrolidine-based system was attempted. The energy difference between the transition states for the (R,R)- and (S,S)-products in the azetidine system is higher, by 0.89 kcal mol⁻¹, than the energy difference in the pyrrolidine system (see the Supporting Information). This finding suggests that the azetidine-based catalyst can afford higher enantioselectivity than the pyrrolidine-based catalyst. This outcome is in accordance with the experimentally observed result.

The chemical structure and physical properties of the CHO/ CO₂ copolymer formed at 10 °C (Table 1, entry 14) were investigated. Previous studies demonstrated that stereochemical information of copolymers can be conveniently collected by ¹³C NMR spectroscopy.^{[20] 13}C NMR signals of poly[cyclohexene oxide-alt-carbon dioxide], in the carbonyl region, were split into two parts: $\delta = 153.7$ and 153.3–153.1 ppm. The large peak at $\delta = 153.7$ ppm was assigned to isotactic diads, whereas the peaks at $\delta = 153.3 - 153.1$ ppm were attributed to syndiotactic diads. In this case, the absence of any peak at $\delta = 153.3$ -153.1 ppm, as shown in Figure 3 (a), indicated clearly that isotactic diads were absolutely predominant in this asymmetric copolymerization of CO₂ and CHO. The ¹³C NMR spectrum, in the carbonyl region, of the copolymer was also consistent with the excellent enantioselectivity (up to 93.3% ee). In addition, the ¹H NMR spectrum of the copolymer in Figure 3(b) shows that the chemoselectivity was also outstanding. The completely alternating structure (>99% carbonate linkage) of the PCHC was confirmed by the absolute predominance of a methine proton peak at $\delta = 4.62$ ppm (assigned to carbonates), and the absence of a methine proton peak around $\delta = 3.45$ ppm (attributed to a polyether from homopolymerization of the CHO).^[21] Differential scanning calorimetry analysis of the copolymer showed that a high crystallization endothermic peak was observed at 240 $^\circ\text{C},$ implying that the PCHC with over 90% enantioselectivity exhibited crystallization.^[8]



Figure 3. a) The carbonyl region of ¹³C NMR and b) ¹H NMR spectrum of poly(cyclohexane carbonate) in Table 1, entry 14.

Chem. Eur. J. 2014, 20, 1–6 www.chemeurj.org

In conclusion, a novel ligand with the azetidine ring shows excellent enantioselectivity for the catalytic asymmetric copolymerization of CO_2 and CHO catalyzed by dinuclear zinc(II). The salient features of this catalytic system include: 1) The alternating copolymerization required only a catalytic amount of the chiral ligand without the presence of stoichiometric amounts of additional chiral induction agents; 2) this catalytic system needed only one atm pressure and room temperature; 3) excellent enantioselectivity, very high yields, and relatively high molecular weights were obtained. The application of this ligand for other asymmetric transformations, as well as the determination of the precise structure of the active species for CHO/CO₂ copolymerization, is currently underway in our labo-

Experimental Section

ratory.

General procedure for the copolymerization of CO₂ and CHO

In a flame-dried Schlenk tube, a solution of diethylzinc (0.20 mL, $1.0\;mol\,L^{-1}$ in hexane, 0.20 mmol) was added to a solution of the chiral ligand 9 (61.2 mg, 0.1 mmol) in dry toluene (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 30 min. Then a solution of dry ethanol (0.04 mL, 1.0 mol L⁻¹ in toluene) was added to the mixture. The solution was stirred at ambient temperature for an additional 15 min, and then cyclohexene oxide (0.2 mL, 2.0 mmol) was introduced. Carbon dioxide was bubbled into the solution whilst stirring at the necessary reaction temperature for 36 h. The mixture was then cooled/heated to room temperature. The mixture was diluted with CH₂Cl₂ (40 mL), and washed with aqueous HCl (1 mol L⁻¹, 3×20 mL) and brine (2 × 20 mL). The organic layer was dried over Na₂SO₄ and concentrated to 5 mL by vacuum evaporation. The copolymer was precipitated by adding MeOH (40 mL), filtered, washed with MeOH, and dried in vacuo to a constant weight. Analysis of the copolymer by gel-permeation chromatography gave molecular weight and molecular-weight distribution.

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4



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COMMUNICATION

Copolymers

Y.-Z. Hua, L.-J. Lu, P.-J. Huang, D.-H. Wei, M.-S. Tang, M.-C. Wang,* J.-B. Chang*

Highly Enantioselective Catalytic System for Asymmetric Copolymerization of Carbon Dioxide and Cyclohexene Oxide



Highly enantioselective copolymeriza-

tion of carbon dioxide with cyclohexene oxide has been achieved under very mild conditions (1 atm CO_2 , room temperature; see scheme, ee = enantiomeric excess). Intramolecular dinuclear zinc complexes containing four-membered rings have been used to catalyze this transformation, affording completely alternating polycarbonates with excellent enantioselectivity (up to 93.8% *ee*), a high M_n value of 28600, and a relatively narrow polydispersity (M_w/M_n ratio) of 1.43.

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