Asymmetric amplification in asymmetric alternating copolymerization of cyclohexene oxide and carbon dioxide†

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Asymmetric amplification in the copolymerization of cyclohexene oxide and carbon dioxide was demonstrated using chiral zinc complexes, prepared from diethylzinc, diphenyl(pyrrolidin-2-yl)methanol, and ethanol.

In 1986, Kagan and his coworkers reported the first example of nonlinear phenomenon in asymmetric catalysis.[1] They illustrated that the relationship between the enantiomeric excess (ee) of a chiral ligand and that of the product in Sharpless epoxidation of geraniol gave a convex curve deviated from the linearly correlated straight line. Such a positive nonlinear phenomenon is also called "asymmetric amplification", and a variety of reactions has been reported up to the present.[2] In principle, this phenomenon originates in the association of several chiral molecules, which induces diastereomeric interaction and affects the reactivity of active species.

Recently, we have reported the asymmetric alternating copolymerization of cyclohexene oxide and CO_2 using a catalytic amount of (S,S)-**1**, which was produced from a mixture of (S,S)-**2** and ethanol, to give an optically active poly(cyclohexene oxide-*alt*-CO_2) of 80% ee (Scheme 1).[3,4] The zinc complex (S,S)-**2** was prepared by the reaction of an equimolar amount of Et_2Zn and a chiral amino alcohol [(S)-diphenyl(pyrrolidin-2-yl)methanol, (S)-**3**-H], and was shown to form a dimeric structure by X-ray analysis.[4c] Based on the previous reports about the organozinc–chiral amino alcoholate complexes such as dialkylzinc–DAIB complexes

[DAIB = (−)-3-*exo*-(dimethylamino)isoborneol],[2d,2e] an employment of non-enantiopure **3**-H is anticipated to cause the formation of homochiral and heterochiral zinc dimers which would trigger off the nonlinear phenomenon in the copolymerization. Herein, we report the asymmetric amplification in the copolymerization of cyclohexene oxide and CO_2.

First, we investigated the effects of ee of the chiral amino alcohol **3**-H on the asymmetric alternating copolymerization. The copolymerization was carried out by treatment of cyclohexene oxide with CO_2 (30 atm) in the presence of a mixture of Et_2Zn (5.0 mol%), **3**-H (5.0 mol%) and ethanol (2.0 mol%) to give the completely alternating copolymer.[5] The catalyst system with enantiopure (S)-**3**-H gave the copolymer in quantitative yield and the ee of the diol unit of the copolymer was 77% (Fig. 1). This result was comparable to the previous one when isolated (S,S)-**1** was used as a catalyst.[4c] On the other hand, the zinc complex produced from racemic **3**-H had lower catalytic activity (29% yield). As clearly illustrated in Fig. 1, a chemical yield was improved in proportion to increase in ee of **3**-H, and the ee of diol unit was always higher than the one estimated from a linear correlation (broken line). Although its size was not so large, asymmetric amplification operated in the alternating copolymerization. To our knowledge, this is a first example of nonlinear phenomenon in the asymmetric synthesis of optically active polymers with main-chain chirality.[6]

The structure of the zinc complex obtained from an equimolar mixture of Et_2Zn and racemic **3**-H was analyzed by an X-ray diffraction (Fig. 2).‡ The obtained complex was a heterochiral zinc dimer (R,S)-**2**: monomeric zinc complexes, [(S)-**3**]ZnEt and [(R)-**3**]ZnEt, did not recognize themselves but recognized each other to form the heterochiral (R,S)-**2**.[7] The heterochiral zinc dimer (R,S)-**2** thus obtained differs from the homochiral (S,S)-**2**[4c] in the following points. (i) The two ethyl groups on the zinc centers of
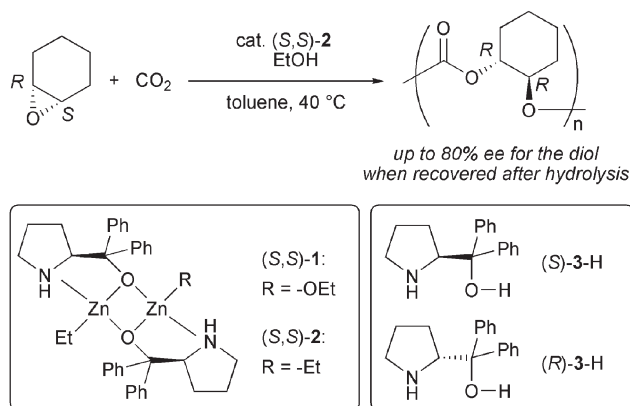
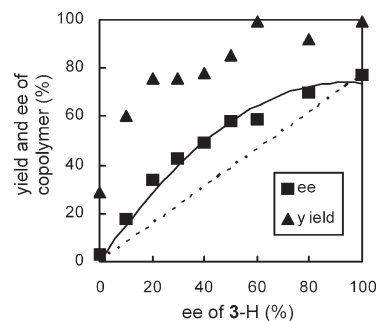Scheme 1 Asymmetric alternating copolymerization of cyclohexene oxide and CO_2.

Fig. 1 Nonlinear phenomenon in the asymmetric alternating copolymerization of cyclohexene oxide and CO_2.
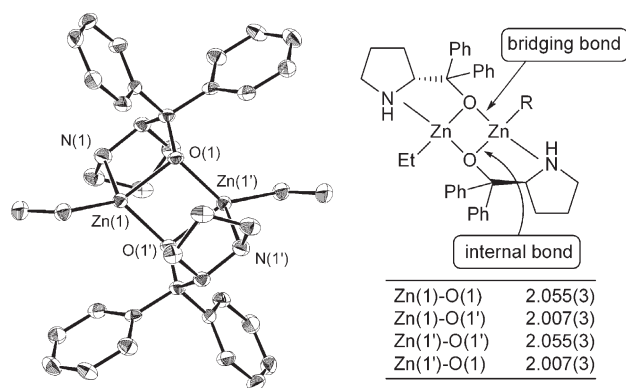
Fig. 2 ORTEP drawing of (*R*,*S*)-**2** with thermal ellipsoids shown at 50% probability level. All hydrogen atoms are omitted for clarity. Equivalent atoms generated by symmetric transformations are distinguished by prime.

Zn(1)-O(1)	2.055(3)
Zn(1)-O(1')	2.007(3)
Zn(1')-O(1')	2.055(3)
Zn(1')-O(1)	2.007(3)

(*R*,*S*)-**2** are oriented in an *anti* direction with respect to the central Zn_2O_2 four-membered ring, while the two ethyl groups in (*S*,*S*)-**2** have *syn* orientation. (ii) The two bridging Zn–O bonds [2.007(3) Å for Zn(1)–O(1') and Zn(1')–O(1)] in (*R*,*S*)-**2** are shorter than those [2.0242(15) and 2.0355(15) Å] in (*S*,*S*)-**2**.[4c] (iii) The two bridging bonds in (*R*,*S*)-**2** are distinctly shorter than the two internal Zn–O bonds [2.055(3) Å], while the corresponding four bonds in (*S*,*S*)-**2** are very close each other. These structural differences between heterochiral and homochiral zinc dimers clearly show the higher stability and the more preferable formation of heterochiral zinc dimer than homochiral one, as is frequently observed in the chiral β-amino alcohol-R_2Zn dinuclear complexes.

In order to further investigate the preferable formation of heterochiral zinc dimer, the copolymerization was carried out using an equimolar mixture of isolated (*S*,*S*)-**2** and (*R*,*R*)-**2** as an initiator precursor. The copolymer was obtained in 43% yield which is significantly lower than that achieved using only isolated (*S*,*S*)-**2** as an initiator precursor. Thus, this result clearly indicates that homochiral zinc dimers do dissociate into monomeric zinc complexes under the reaction conditions to form a more stable, but less active heterochiral zinc dimer.

The ^{13}C NMR spectra of the copolymers obtained give us insight into the polymerization mechanism. Fig. 3 shows the carbonyl region of ^{13}C NMR spectra of (a) the copolymer obtained with racemic **3**-H as a ligand, and (b) the copolymer of
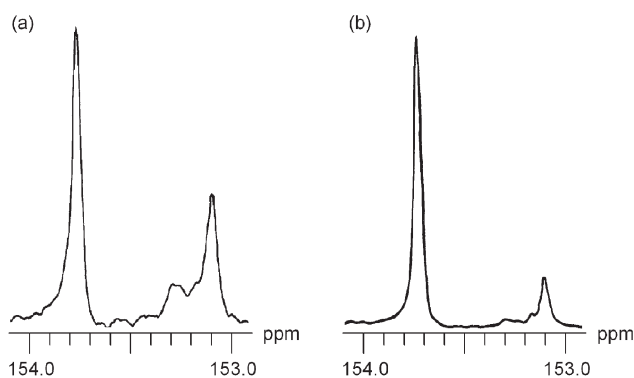

Fig. 3 Carbonyl region of ^{13}C NMR spectra of (a) the copolymer obtained using racemic **3**-H as a ligand, and (b) the copolymer obtained using (*S*,*S*)-**1** as an initiator.

80% ee obtained with (*S*,*S*)-**1**.[4c] As illustrated, the signals are not identical with each other, demonstrating the difference in tacticity.[4b,8] If a polymer chain had been created by a single monomeric zinc complex, the copolymers (a) and (b) with the same tacticity should be obtained regardless of ee of a ligand because monomeric zinc complexes [(*R*)-**3**]ZnR′ and [(*S*)-**3**]ZnR′ (R′ = Et-, EtO-, or polymer chain) are enantiomers with the same reactivity and selectivity. Thus, it can be concluded that the monomeric zinc species do not grow the polymer chain independently.[4c]

By integrating these experimental results, the stability difference between heterochiral and homochiral zinc dimers should be the origin of asymmetric amplification, as is often the case with the reported nonlinear phenomenon.[1,2] Because the epoxide binding to zinc center is necessary for the ring-opening,[9] the dissociation of both or either of the two Zn–O bridging bonds is required for the enchainment event. Accordingly, strong bridging bond likely make the heterochiral zinc dimer less active for the polymerization. When nonracemic but not enantiomerically pure **3**-H is employed, the minor enantiomer is selectively *trapped* by the major enantiomer to form the more stable heterochiral zinc dimer. As a result, the polymerization system gains a net increase in enantiopurity of active zinc species, thus leading to the asymmetric amplification. Tacticity difference of the copolymers can plausibly be attributed to the involvement of the diastereomeric interaction between two chiral monomeric zinc species in the ring-opening event. That is, bimetallic enchainment mechanism reported in the previous literatures[10] nicely accounts for our system, although it is unclear whether two monomeric zinc species works cooperatively[10a] or dimeric form is maintained during the polymerization.[9,10b,11,12]

In conclusion, we report asymmetric amplification in the copolymerization of cyclohexene oxide and CO_2 using zinc–chiral amino alcohol complexes. Further efforts are directed towards kinetic studies to understand further the mechanistic aspect.

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Notes and references

‡ *Crystal data.* $C_{19}H_{23}NOZn$, *M* = 346.75, monoclinic, *a* = 12.1430(7), *b* = 11.2307(6), *c* = 12.2015(7) Å, β = 101.6860(10)°, *U* = 1629.48(16) Å³, *T* = 130 K, space group *P*2(1)/*n*, *Z* = 4, μ(Mo–Kα) = 1.508 mm^{-1}, 11160 reflections measured, 3723 unique (R_{int} = 0.0247) which were used in all calculations. The final $wR(F^2)$ was 0.1648 (all data). CCDC 254118. See http://www.rsc.org/suppdata/cc/b4/b417973k/ for crystallographic data in .cif or other electronic format.

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5 Ideal molar ratio of EtOH/Zn should be 0.5. However, the optimum condition for *in situ* preparation of the zinc initiator was accomplished when the ratio was 0.4, see reference 4c. Polymerization results are described in ESI.

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