Enantioselective terpolymerization of racemic and meso-epoxides with anhydrides for preparation of chiral polymers

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The preparation of stereochemistry- and sequence-defined polymers, in which different monomer units are arranged in an ordered fashion just like biopolymers, is of great interest and has been a long-standing goal for chemists due to the expectation of unique macroscopic properties. Here, we describe the enantioselective terpolymerization of racemic terminal epoxides, meso-epoxides, and anhydrides mediated by the privileged chiral dinuclear Al(III) catalyst system, to afford optically active polyester terpolymers with either gradient or random distribution as determined by the epoxides employed during their preparation. The enantioselective terpolymerization of racemic tert-butyl glycidyl ether (rac-TBGE) and cyclopentene oxide with phthalic anhydride (PA) or naphthyl anhydride (NA) gives novel gradient polymers, in which the crystallization behavior varies continuously along the main chain, due to the decrement of one ester component and the increment of the other occurring sequentially from one chain end to the other. In contrast, the enantioselective terpolymerization of rac-TBGE and meso-epoxide (cyclohexene oxide, 3,4-epoxytetrahydrofuran, or 1,4-dihyronaphthalene oxide) with an anhydride (PA or NA) provided chiral statistical terpolymers with the random distribution of two kinds of ester units, resulting in a material possessing a mixed glass transition temperature. The present study therefore provides a convenient route to chiral polyesters bearing a range of physical and degradability properties.

Significance

The accurate control of macromolecular stereochemistry and sequences is a powerful strategy to manipulate polymer properties. The enantioselective terpolymerization of anhydrides with two kinds of substituted epoxides exhibiting different reactivities and stereogenic centers offers the accessibility to stereochemistry- and sequence-defined polymers. In this paper, we utilize the privileged chiral dinuclear Al(III) catalyst for the enantioselective terpolymerization of cyclic anhydrides, racemic epoxides, and meso-epoxides, to prepare optically active terpolymers with gradient or random distributions. In particular, the crystallization behaviors of the resultant gradient terpolymers vary continuously along the main chain, due to the decrement of one ester component and the increment of the other occurring sequentially from one chain end to the other.

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to substituted epoxides allow for the preparation of stereoregular polymers with main-chain chirality through enantioselective polymerization (15, 16). In 2016, we achieved the asymmetric copolymerization of achiral meso-epoxides and cyclic anhydrides to afford isotactic polyesters with a completely alternating nature (17). Recently, enantiopure bimetallic aluminum or cobalt complexes were discovered to be highly active in catalyzing the enantioselective resolution copolymerization of racemic epoxides and anhydrides, affording highly isotactic polyesters with exceptional levels of enantioselectivity, and with kinetic resolution coefficients ($K_{\text{res}}$) of $>300$, in addition to selectivity factors (s-factors) of $>300$ (18). In the present paper, we utilize the privileged chiral dinuclear aluminum catalyst for the enantioselective terpolymerization of cyclic anhydrides, racemic epoxides, and meso-epoxides to prepare optically active terpolymers with gradient or random distribution, as determined by the monomers employed during their preparation (Fig. 1).

Results and Discussion

Screening Highly Enantioselective Catalysts for the Copolymerization of Anhydrides with Racemic or Meso-Epoxides. Compared with the asymmetric copolymerization of meso-epoxides with anhydrides, the enantioselective resolution copolymerization of racemic terminal epoxides exhibits a significant difference in chiral induction on the epoxide ring-opening process. As a result, the preparation of isotactic-enriched polyesters from the aforementioned enantioselective copolymerization reactions triggered just by one kind of catalyst is extremely challenging. In previous studies, various dinuclear catalysts based on the bimetallic synergistic effect enabled the preparation of stereoregular polymers through enantioselective ring-opening (co)polymerization of epoxides (16–20). The chirality of both the axial linker and the diamine backbones of the ligand were responsible for the chiral induction of these polyesters. Also, a subtle modification of the phenolate ortho-substituents on the ligand resulted in marked changes for both the catalytic activity and enantioselectivity. As far as epoxides/anhydrides copolymerization, we have discovered that enantiopure binaphthol-linked dinuclear aluminum complexes 1a and 1b were more efficient in the enantioselective resolution copolymerization of racemic terminal epoxides and anhydrides to produce isotactic polyesters with extraordinary levels of enantioselection (18), while hydrogenated binaphthol-linked bimetallic aluminum complexes 2a and 2b could effectively catalyze the asymmetric copolymerization of meso-epoxides with anhydrides to afford polyesters with ee (enantioimeric excess) values of up to 99% (19). Moreover, for the two types of enantioselective copolymerization reactions, the enantioselectivity and polymerization rate were found to be significantly affected by the axial linker, the chiral diamine structure, and the phenolate ortho-substituents present on the ligand. Therefore, our goal is to screen versatile and enantioselective catalysts predominantly focuses on enantiopure dinuclear aluminum complexes 1 and 2 bearing a configuration-matched axial linker with chiral diamine backbones.

Due to their relatively high reactivities, racemic tert-butyl glycidyl ether (rac-TBGE) and cyclohexene oxide (CHO) were chosen as the model racemic terminal epoxide and meso-epoxide, respectively, in the copolymerization with phthalic anhydride (PA) as a model anhydride. Although binaphthol-linked dinuclear aluminum complex (S,S,S,S,S)-1a in conjunction with PPNCI [PPN = bis(triphenylphosphine)iminium] showed a high activity and enantioselectivity for the resolution copolymerization of racemic TBGE and PA, affording the corresponding polyester with 99% ee (Table 1, entry 1); unfortunately, when this catalyst system was applied in the asymmetric copolymerization of CHO with PA, the resultant copolymer with a completely alternating structure exhibited an enantioselectivity of only 81% ee with the (S,S)-configuration (Table 1, entry 2). Fortunately, in comparison with (S,S,S,S,S)-1a, (S,S,S,S)-2b bearing isopropyl groups on the phenolate ortho-position showed a relatively lower s-factor of 113 in catalyzing the rac-TBGE/PA copolymerization reaction to give an isotactic polyester with 95% ee, but a higher enantioselectivity in mediating the CHO/PA copolymerization reaction, affording the corresponding polyester in 98% ee (Table 1, entries 3 and 4). Hydrogenated binaphthol-linked dinuclear aluminum complexes 2a and 2b were also tested for both enantioselective transformations. Activated by PPNCI, (S,S,S,S,S)-2a was highly active in catalyzing both the rac-TBGE/PA and CHO/PA copolymerization reactions; however, the resulting polyesters had lower ee values of 85% and 83%, respectively (Table 1, entries 5 and 6). Although an enhanced enantioselection of 98% ee was observed upon the replacement of (S,S,S,S,S)-2a with (S,S,S,S,S)-2b for the CHO/PA copolymerization reaction, the same catalyst system gave a low s-factor of 10 for the rac-TBGE/PA copolymerization reaction (Table 1, entries 7 and 8). Therefore, only the (S,S,S,S,S)-1b–based catalyst system meets the requirement for modulating both of the enantioselective copolymerization reactions and providing highly isotactic polyesters (>95% ee) with a perfectly alternating structure and a low polydispersity index.

With the versatile, enantioselective catalyst system (S,S,S,S,S)-1b/PPNCI in hand, a wide range of racemic and meso-epoxides were tested in the copolymerization reaction with anhydrides. Various glycidyl ethers, such as ethyl glycidyl ether (ETGE), isopropyl glycidyl ether (IPGE), phenyl glycidyl ether (PGE), and furfuryl glycidyl ether (FurGE) were able to copolymerize with PA, exhibiting good enantioselectivities with s-factors between 39 and 54 (Table 1, entries 9 through 12). When activated by PPNCI, (S,S,S,S,S)-1b was found to be efficient in copolymerizing PA with various aliphatic racemic terminal epoxides, such as propylene oxide (PO), 1,2-epoxybutane (BO), and 1,2-hexylene oxide (HO), affording the corresponding polyesters with s-factors in the range of 23 to 29 (Table 1, entries 13 through 15). The enantioselective resolution copolymerization

![Fig. 1. Enantiopure dinuclear aluminum complex-mediated enantioselective terpolymerization of racemic terminal epoxides, meso-epoxides, and anhydrides to prepare chiral polyesters with gradient or random distribution.](image-url)
preferentially consumes the aliphatic (S)-epoxide over its (R)-configuration enantiomer. This is in contrast to the copolymerization systems employing glycidyl ether derivatives, in which the (R)-epoxide is consumed. It should be noted that the incorporation of (R)-configuration glycidyl ethers into polyes
ters affords an ester unit with the (S)-configuration. However, hydrolysis of the resulting polyes
ters produces (R)-configuration diols.

Table 1. Outcomes of the enantioselective copolymerization reactions of epoxides and anhydrides mediated by various enantiopure bimetallic aluminum complexes

| Entry | Catalyst | Monomers | Time, h | Conv., % | TOF†, h⁻¹ | $M_n$, kg/mol | $D$, ‡ | ee(epo), † | K_rel, † | ee(poly), ‡ | s-factor‡ |
|-------|----------|----------|--------|----------|------------|--------------|------|-----------|----------|------------|--------|
| 1     | (S,S,S,S)-1a | TBGE/PA | 1.1    | 43       | 195        | 13.5         | 1.17 | 75 (S)   | >300     | 99 (R)     | >300   |
| 2     | (S,S,S,S)-1a | CHO/PA  | 18     | 99       | 14         | 10.9         | 1.13 | **        | **       | 81 (S,S)   | **     |
| 3     | (S,S,S,S)-1b | TBGE/PA | 2      | 48       | 120        | 14.7         | 1.16 | 88 (S)   | 122      | 95 (R)     | 113    |
| 4     | (S,S,S,S)-1b | CHO/PA  | 4      | 98       | 61         | 14.4         | 1.19 | **        | **       | 97 (S,S)   | **     |
| 5     | (S,S,S,S)-2a | TBGE/PA | 1.9    | 44       | 116        | 13.9         | 1.15 | 68 (S)   | 28       | 85 (R)     | 25     |
| 6     | (S,S,S,S)-2a | CHO/PA  | 1.3    | 96       | 184        | 13.8         | 1.13 | **        | **       | 83 (S,S)   | **     |
| 7     | (S,S,S,S)-2b | TBGE/PA | 2.3    | 38       | 83         | 10.7         | 1.17 | 82 (S)   | 13       | 73 (R)     | 10     |
| 8     | (S,S,S,S)-2b | CHO/PAX | 1      | 99       | 250        | 15.1         | 1.14 | **        | **       | 98 (S,S)   | **     |
| 9     | (S,S,S,S)-1b | FurGE/PA | 2     | 48       | 120        | 13.6         | 1.17 | 82 (S)   | 43       | 88 (R)     | 39     |
| 10    | (S,S,S,S)-1b | FurGE/PA | 2      | 45       | 113        | 10.4         | 1.14 | 75 (S)   | 52       | 91 (R)     | 47     |
| 11    | (S,S,S,S)-1b | IPGE/PA | 2      | 47       | 118        | 11.3         | 1.13 | 81 (S)   | 55       | 91 (R)     | 53     |
| 12    | (S,S,S,S)-1b | IPGE/PA | 2      | 46       | 115        | 13.5         | 1.15 | 77 (S)   | 46       | 90 (R)     | 44     |
| 13    | (S,S,S,S)-1b | PO/PA   | 3      | 42       | 70         | 7.7          | 1.21 | 62 (R)   | 24       | 85 (S)     | 23     |
| 14    | (S,S,S,S)-1b | BO/PA   | 3      | 40       | 67         | 8.9          | 1.16 | 58 (R)   | 26       | 86 (S)     | 24     |
| 15    | (S,S,S,S)-1b | HO/PA   | 4      | 46       | 58         | 10.4         | 1.12 | 74 (S)   | 32       | 86 (S)     | 29     |
| 16    | (S,S,S,S)-1b | TBGE/NA | 8      | 41       | 26         | 9.7          | 1.17 | 66 (S)   | 77       | 94 (R)     | 64     |
| 17    | (S,S,S,S)-1b | CPO/PA  | 8      | 43       | 27         | 4.6          | 1.33 | **        | **       | 98 (S,S)   | **     |
| 18    | (S,S,S,S)-1b | CPO/PA  | 5      | 90       | 45         | 13.4         | 1.17 | **        | **       | 98 (S,S)   | **     |
| 19    | (S,S,S,S)-1b | CEO/PA  | 10     | 99       | 25         | 15.3         | 1.19 | **        | **       | 98 (S,S)   | **     |
| 20    | (S,S,S,S)-1b | CBO/PS  | 10     | 93       | 23         | 10.3         | 1.21 | **        | **       | 97 (S,S)   | **     |
| 21    | (S,S,S,S)-1b | CDO/PA  | 12     | 53       | 11         | 7.5          | 1.16 | **        | **       | 98 (S,S)   | **     |
| 22    | (S,S,S,S)-1b | CHO/NA  | 8      | 89       | 25         | 10.7         | 1.15 | **        | **       | 98 (S,S)   | **     |
| 23    | (S,S,S,S)-1b | CPO/NA  | 18     | 53       | 7          | 4.4          | 1.32 | **        | **       | 97 (S,S)   | **     |
| 24    | (S,S,S,S)-1b | CPO/NA  | 10     | 92       | 23         | 11.2         | 1.17 | **        | **       | 98 (S,S)   | **     |

*All reactions were performed at 25 °C. For entries 1, 3, 5, 7, and 9 through 16, the reactions were performed under the following conditions: epoxide/anhydride/catalyst/PPNCI/toluene = 500/250/1/2/250 (molar ratio). For entries 2, 4, 6, 8, and 17 through 24, reactions were performed using an excess of epoxide, where meso-epoxide/anhydride/catalyst/PPNCI = 1,000/250/1/2 (molar ratio).
†Turnover frequency (TOF) = mole of product (polyester)/mole of catalyst per hour.
‡Determined using gel permeation chromatography in tetrahydrofuran, calibrated with polystyrene.
§Measured by derivatizing the unreacted epoxide using 2-mercaptobenzothiazole and then determining the ee via chiral HPLC analysis, or determining the ee via chiral HPLC analysis directly.
‖Calculated using $K_{rel} = \ln[(1-\text{c})(1-e_{(\text{epo})})]/\ln[(1-\text{c})(1+e_{(\text{epo})})]$, where c is the epoxide conversion.
*Measured by hydrolyzing the polymer and analyzing the resulting diol via chiral GC or derivatizing the resulting diol using acetic anhydride or benzoyl chloride and then determining the ee via chiral GC or HPLC analysis.
**Calculated using s-factor = ln[(1-c)(1+e_{(\text{poly})})]/ln[(1-c)(1-e_{(\text{poly})})], where c is the conversion of the epoxide monomer.
***No result.
Moreover, with rac-TBGE as the epoxide monomer, naphthyl anhydride (NA) was employed in the enantioselective copolymerization reaction, affording the corresponding polyester with 94% ee (Table 1, entry 16). Notably, using the (S,S,S,S,S)-1b/PPNCl catalyst system, numerous meso-epoxides (3,4-epoxytetrahydrofuran [COPO], cis,2,3-epoxybutane [CBO], 1,2-epoxy-4-cyclohexene [CEO], and 1,4-dihydronaphthalene oxide [CDO]) copolymerized with PA or NA, displaying good reactivities and enantioselectivities and producing the corresponding (S,S)-polymers with a complete alternating structure, low molecular weight distribution, and >97% ee (Table 1, entries 17 through 24).

Synthesis of Chiral Terpolysters with Gradient Distribution. The synthesis of sequence-defined polymers in which monomer units of different chemical natures are arranged in an ordered fashion has intrigued chemists due to their unique macroscopic properties (21). Among the reported synthetic methods for controlling monomer sequences in polymers, catalyst-site-controlled coordination polymerization is commonly utilized to produce high-performance materials with various topological microstructures by changing the coordination environment of the corresponding active species to adjust the reactivity ratios of monomer couples (6, 7). In the case of the present study, we expect to obtain sequence-defined chiral terpolysters with adjustable properties over a wide range through the enantioselective terpolymerization of racemic and meso-epoxides.

Using the (S,S,S,S,S)-1b/PPNCl catalyst system, the enantioselective terpolymerization of rac-TBGE, CPO, and PA was performed at 25 °C. The relative compositions of two kinds of ester units in resultant terpolymers could be easily tuned by varying the epoxide ratios in the feedstock. It should also be noted here that the enantioselectivities of two types of ester units in the terpolymers were identical to those of the copolymers resulting from the enantioselective copolymerization of PA with racemic TBGE or CPO. For example, the ee values of cyclopentane-1,2-diol and 3-(tert-butoxy)propene-1,2-diol hydrolyzed from the terpolymers resulting from various epoxide feed ratios (Table 2) were 97% for the (S,S)-configuration and 95% for the (R)-configuration. These results indicate that the terpolymerization process has no effect on the enantioselective ring-opening steps of either the racemic or meso-epoxides.

The reactivity ratio of monomers is an important parameter for understanding the reaction mechanism and microstructure of the resulting terpolymers. Since rac-TBGE has two enantiomers with (R) and (S)-configurations, the enantioselective terpolymerization of rac-TBGE/CPO/PA mediated by the (S,S,S,S,S)-1b/PPNCl catalyst system was evaluated using Fineman–Ross plots for the terpolymerization reactions of (S)-TBGE/CPO/PA and (R)-TBGE/CPO/PA to gain insight into the reactivity ratios of the monomers. More specifically, the reactivity ratios of (S)-TBGE and CPO were calculated to be \( r_{(S),TBGE} \approx 0 \) and \( r_{CPO} = 109 \) according to the Fineman–Ross plot (Fig. 2A). This result indicates a significantly higher activity for the formation of (CPO-alt-PA)–(CPO-alt-PA) linkages over (TBGE-alt-PA)–(TBGE-alt-PA) linkages owing to the lower reaction rate of (S)-TBGE compared to CPO. Furthermore, the Fineman–Ross plot of the (R)-TBGE/CPO/PA terpolymerization reaction gave reactivity ratios of \( r_{(R),TBGE} = 8.7 \) and \( r_{CPO} = 0.24 \) for (R)-TBGE and CPO (Fig. 2B). This result revealed that the terpolymerization reaction preferentially formed (TBGE-alt-PA)–(TBGE-alt-PA) linkages in the initial stages due to the higher reactivity of (R)-TBGE. Notably, the resulting terpolymers presented different melting temperatures with variation in the (TBGE-alt-PA) unit content. More specifically, when the content of the (TBGE-alt-PA) ester unit was 95%, the terpolymers exhibited a melting temperature of 53 °C and a \( T_m \) of 92 °C, which is close to the \( T_m \) of the isotactic Poly(TBGE-alt-PA) copolymers (Fig. 3, curves A and B). As the (TBGE-alt-PA) ester unit content was reduced, the \( T_m \) resulting from the (TBGE-alt-PA)–(TBGE-alt-PA) linkage remained and another \( T_m \) attributed to the (CPO-alt-PA)–(CPO-alt-PA) ester linkage appeared. Indeed, when the (TBGE-alt-PA) ester unit...
content was 52%, the terpolymer exhibited two melting peaks, at 92 and 177 °C (Fig. 3, curve D). Furthermore, upon increasing the (CPO-alt-PA) ester unit content to 80%, only a T\textsubscript{m} of 244 °C was detected, and this value is close to that of the isotactic poly(CPO-alt-PA) copolymer (Fig. 3, curves F and G).

To explore the variation in the polymer microstructure during the terpolymerization process, intermittent sampling experiments were conducted with the rac-TBGE/CPO/PA = 2/1/2 (molar ratio) feedstock in toluene to monitor the ester unit content and the thermal properties. As is shown in Fig. 4, Left, rac-TBGE copolymerized with PA in the initial stages due to the higher reactivity of (R)-TBGE compared to that of CPO. Upon increasing the PA conversion, the (TBGE-alt-PA) ester unit content exhibited a gradual downward trend accompanied by an increase in the (CPO-alt-PA) ester content, which corresponds to reactivity ratios of r\textsubscript{(R)-TBGE} = 8.7 and r\textsubscript{CPO} = 0.24. Meanwhile, the crystalline behavior varied continuously as main-chain propagation progressed. More specifically, terpolymers with a 86% content of (TBGE-alt-PA) ester unit exhibited a T\textsubscript{g} of 42 °C and a T\textsubscript{m} of 94 °C with a ΔH\textsubscript{m} of only 4.7 J/g (Fig. 4, Right, curve A). When the complete conversion of PA was achieved, the resulting terpolymers exhibited two T\textsubscript{ms} of 92 and 177 °C (Fig. 4, Right, curve D), thereby demonstrating that the two kinds of ester units in the resulting terpolymers exhibit a random sequence distribution. Due to the inherent structure differences between the two kinds of ester units, the resulting statistical terpolymer is a typically gradient distribution structure.

Moreover, the (S,S,S,S,S)-1b/PPNCl–mediated rac-TBGE/CPO/NA enantioselective polymerization reaction also afforded chiral gradient terpolymers. In this terpolymerization system, a significant difference was observed between the reaction rates of (R)-TBGE and CPO during terpolymerization with NA (r\textsubscript{(R)-TBGE} = 12.3 and r\textsubscript{CPO} = 0.13) (SI Appendix, Fig. S1).

**Synthesis of Chiral Terpolyesters with Random Distributions.** In contrast to the significant difference in reactivities of (R)-TBGE versus CPO during terpolymerization with PA or NA using the (S,S,S,S)-1b/PPNCl catalyst system, CHO, COPO, and CDO have reactivities comparable to (R)-TBGE. For example, in the enantioselective terpolymerization of rac-TBGE/CHO/PA, (S)-TBGE exhibits no or very low activity in the copolymerization reaction with PA, and a comparable reactivity ratio (r\textsubscript{(R)-TBGE} = 1.10 and r\textsubscript{CHO} = 0.38) was found for the reaction of (R)-TBGE with CHO during terpolymerization with PA at 25 °C (Fig. 5).

This result indicates that the two kinds of ester units in the resulting terpolymers exhibit a random sequence distribution. Due to the inherent structure differences between the two kinds of ester units, the resulting statistical terpolymer is a typically gradient distribution structure.
amorphous material with a mixed $T_g$ of 87 °C, although the two ester units exhibited high enantioselectivities of >95% ee (Table 3, entry 1). In addition, it was possible to adjust the $T_g$ by altering the $\text{rac-TBGE}/\text{CHO}$ feed ratio (Table 3, entries 2 and 3).

Moreover, the Fineman–Ross plots for the (R)-TBGE/CHO/NA, (R)-TBGE/COPO/PA, (R)-TBGE/COPO/NA, and (R)-TBGE/CDO/PA terpolymerization reactions suggest relatively similar reactivities during their copolymerization with PA (SI Appendix, Figs. S2–S5), thereby leading to the production of chiral statistical terpolymers with mixed $T_g$s (Table 3, entries 4 through 7), in which two kinds of ester units are distributed in the main chain with probability. Taking the $\text{rac-TBGE}/\text{COPO}/\text{PA}$ terpolymerization process as an example, a comparable reactivity ratio ($r_{\text{TBGE}} = 1.10$ and $r_{\text{COPO}} = 0.67$) was observed for (R)-TBGE and COPO in this reaction at 25 °C.

Conclusion

In conclusion, we successfully developed a versatile chiral dinuclear aluminum catalyst system which could trigger the enantioselective copolymerization of cyclic anhydrides with racemic terminal epoxides or meso-epoxides, to produce highly isotactic polyesters with perfectly alternating structures and low polydispersity indices. In addition, the catalyst system was demonstrated to be particularly effective in the enantioselective terpolymerization of racemic terminal epoxides, meso-epoxides, and anhydrides, affording optically active terpolymers with gradient or random sequence distributions, depending on the epoxides used for the reaction. Notably, the terpolymerization process had no influence on the enantioselective ring-opening steps of the racemic epoxides and meso-epoxides. Furthermore, due to the significant differences in the reactivities of TBGE and CPO during their terpolymerization with anhydrides, terpolymers with unique gradient natures were obtained, in which the crystallization behavior varied continuously along the main chain. In contrast, the enantioselective rac-TBGE/CHO/PA, rac-TBGE/CHO/NA, rac-TBGE/COPO/PA, rac-TBGE/COPO/NA, and rac-TBGE/CDO/PA terpolymerization reactions provided amorphous polyesters with random sequence distributions which possessed mixed $T_g$s. The present study therefore provides a convenient route to degradable chiral polyesters with adjustable properties over a wide range. Further investigations will focus on exploring the properties of these chiral terpolymers, in addition to their medicinal application as degradable materials.

Materials and Methods

General Information. All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. All tested epoxides were dried over calcium hydride prior to the use. PPNCI was recrystallized by layering a saturated methylene chloride solution with diethyl ether. PA and NA were purified by sublimation before the use. Complexes 1 and 2 were synthesized according to the literature methods (19).

Representative Procedures for the Enantioselective Copolymerization of Meso-Epoxides and Anhydrides. In a 20-mL flask equipped with a magnetic stirrer, complex (S,S,S,S,S)-1b (0.05 mmol, 1 equivalent [equiv.]), PPNCI (0.10 mmol, 2 equiv.) and anhydride (12.5 mmol, 250 equiv.) were dissolved in meso-epoxide (50 mmol, 1,000 equiv.) in an argon atmosphere. The mixture solution was stirred at 25 °C. After complete conversion of the anhydride, a small amount of the resultant mixture was removed from the flask for $^1$H NMR analysis to quantitatively give the ester linkage content in the obtained copolymer. The remaining was dissolved in 10 mL CH$_2$Cl$_2$. Then, the hydrogen chloride–diethyl ether solution (2 M, 0.1 mL) and an appropriate ethanol were added dropwise into the solution. The mixture solution was heated at 55 °C until the white precipitate was slowly formed. This process was

Fig. 4. (Left) Plots of the (TBGE-alt-PA) and (CPO-alt-PA) unit contents in the resultant terpolymers versus the PA conversion in the rac-TBGE/COPO/PA terpolymerization reaction mediated by the (S,S,S,S)-1b/PPNCI catalyst system (1b/PPNCI/rac-TBGE/COPO/PA/toluene $= 1/2/400/200/400$, molar ratio) at 25 °C. (Right) DSC profiles of the resulting terpolymers at various conversions of PA: (A) 25%, (B) 52%, (C) 77%, and (D) 100%.

Fig. 5. Fineman–Ross plots and kinetic parameters for the (R)-TBGE/CHO/PA terpolymerization reaction mediated by the (S,S,S,S)-1b/PPNCI catalyst system.

Caption for Fig. 5:

(R)-TBGE/CHO/PA

$r(\text{k}_{42}/\text{k}_{43}) = 0.38$

$r(\text{k}_{39}/\text{k}_{42}) = 1.10$

$r(\text{k}_{44}/\text{k}_{42}) = 1.10$

$r(\text{k}_{42}/\text{k}_{44}) = 0.38$

$r(\text{k}_{43}/\text{k}_{42}) = 1.10$

$r(\text{k}_{44}/\text{k}_{43}) = 0.38$

$r(\text{k}_{42}/\text{k}_{44}) = 1.10$

$r(\text{k}_{43}/\text{k}_{44}) = 0.38$

$r(\text{k}_{44}/\text{k}_{43}) = 1.10$

$r(\text{k}_{43}/\text{k}_{44}) = 0.38$

$r(\text{k}_{44}/\text{k}_{43}) = 1.10$

$r(\text{k}_{43}/\text{k}_{44}) = 0.38$

$r(\text{k}_{44}/\text{k}_{43}) = 1.10$
repeated three to five times to completely remove the catalyst and white polymer was obtained by vacuum drying.

Representative Procedures for Enantioselective Resolution Copolymerization of Racemic Epoxides and Anhydrides. In a 20-mL flask equipped with a magnetic stirrer, complex (S,S,S,S,S)-1b (0.05 mmol, 1 equiv.), PPNCl (0.10 mmol, 2 equiv.), anhydride (12.5 mmol, 250 equiv.), and racemic epoxide (20 mmol, 400 equiv.) were dissolved in toluene (25 mmol, 500 equiv.) in an argon atmosphere. The mixture solution was stirred at 25 °C. After an appropriate time, a small amount of the resultant mixture was removed from the flask for 1H NMR analysis to give the conversion of epoxides, ratio of two types of ester units in the terpolymer, and determine the ee value of the unreacted terminal epoxide by chiral HPLC analysis. The hydrogen chloride-diethyl ether solution (2 M, 0.1 mL) was added dropwise after the crude polymer was dissolved in 10 mL CH2Cl2. The solution was precipitated with excess methanol. This process was repeated three to five times to completely remove the catalyst, and white polymer was obtained by vacuum drying.

Representative Procedures for Enantioselective Terpolymerization of Racemic Epoxides, Meso-Epoxides, and Anhydrides. In a 20-mL flask equipped with a magnetic stirrer, complex (S,S,S,S,S)-1b (0.05 mmol, 1 equiv.), PPNCl (0.10 mmol, 2 equiv.), anhydride (20 mmol, 400 equiv.), racemic epoxide (20 mmol, 400 equiv.), and meso-epoxide (10 mmol, 200 equiv.) were dissolved in toluene (20 mmol, 400 equiv.) under an argon atmosphere. After an appropriate time, a small amount of the resultant mixture was removed from the flask for 1H NMR analysis to give the conversion of epoxides, ratio of two types of ester units in the terpolymer, and determine the ee value of the unreacted terminal epoxide by chiral HPLC analysis. The hydrogen chloride-diethyl ether solution (2 M, 0.1 mL) was added dropwise after the crude polymer was dissolved in 10 mL CH2Cl2. The solution was precipitated with excess methanol. This process was repeated three to five times to completely remove the catalyst, and white polymer was obtained by vacuum drying.

Date Availability. The main data supporting the findings of this study are available within the paper and SI Appendix.

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