From *meso*-Lactide to Isotactic Polylactide: Epimerization by B/N Lewis Pairs and Kinetic Resolution by Organic Catalysts

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Ⓢ *Supporting Information*

ABSTRACT: B/N Lewis pairs have been discovered to catalyze rapid epimerization of *meso*-lactide (LA) or LA diastereomers quantitatively into *rac*-LA. The obtained *rac*-LA is kinetically polymerized into poly(L-lactide) and optically resolved D-LA, with a high stereoselectivity k_L/k_D of 53 and an ee of 91% at 50.6% monomer conversion, by newly designed bifunctional chiral catalyst **4** that incorporates three key elements (*β*-isocupreidine core, thiourea functionality, and chiral BINAM) into a single organic molecule. The epimerization and enantioselective polymerization can be coupled into a one-pot process for transforming *meso*-LA directly into poly(L-lactide) and D-LA.

Poly(lactide) (PLA) is one of the most commercially important biodegradable and biocompatible polymers, with a wide array of applications in packaging, microelectronics, and biomedical fields.[1] Crystalline isotactic PLA (*it*-PLA) is produced by either ring-opening polymerization (ROP) of *S,S*-lactide (L-LA) to isotactic poly(L-lactide) (PLLA) or the stereoselective ROP of *rac*-LA by metal-based catalysts or initiators.[2] The emerging organopolymerization of LA offers a metal-free alternative to the PLA products that are free of residual metal contaminates as desired for biomedical or microelectronic applications.[3] The stereoselective organopolymerization of *rac*-LA has been achieved by a phosphazene superbase (^tBu-P$_2$) and bulky N-heterocyclic carbenes (NHCs) at low temperatures,[4] and enantioselective or kinetic resolution polymerization of *rac*-LA by chiral organic catalysts has also been made possible by a cinchona alkaloid[5] and chiral phosphoric acids.[6]

The current industrial PLLA production relies on the large-scale production of L-LA, which is furnished via metal (tin)-catalyzed depolymerization of a low molecular weight (MW) condensation prepolymer of L-lactic acid.[7] However, this process affords a mixture of LA stereoisomers that are predominately L-LA but also a considerable amount of *meso*-LA as a byproduct or waste that needs to be removed from the rest of the LA stream, seriously affecting the economy of the manufacturing of PLLA.[8] In addition, as a possible feedstock-recycling pathway, thermal degradation of PLLA produced many kinds of degradation products including LA diastereomers (*rac*-LA/*meso*-LA = 2/1), cyclic oligomers, and their diastereomers as well as CO$_2$, CO, CH$_3$CHO, and CH$_2$=CHCOOH.[9] Hence, racemization causes a serious problem with the feedstock recycling and the reproduction of PLLA.[10] The optical purity of LA significantly affects the materials properties of the PLLA produced by ROP,

and any incorporation of *meso*-LA into the PLLA product will significantly alter or deteriorate the properties of the PLLA materials such as crystallinity and biodegradation rate.[11]

The ROP of *meso*-LA typically forms predominantly atactic, amorphous PLA,[12] but the stereoselective ROP of *meso*-LA has led to syndiotactic PLA (*st*-PLA)[13] or amorphous heterotactic PLA.[14] The crystalline *st*-PLA has a melting-transition temperature (T_m) of ~150 °C,[13f] which is about 20−30 °C lower than that of *it*-PLA, thus an inferior material. Hence, it is of great interest to be able to catalytically isomerize *meso*-LA to *rac*-LA.[15] However, the epimerization under base-catalyzed homogeneous conditions is controlled by the equilibrium between *meso*-LA and *rac*-LA, achieving only an equilibrium mixture;[8] citing the state-of-the-art example here, epimerization of *meso*-LA by sodium ethylhexanoate (0.05%) in bulk at 160 °C for 15 h afforded a mixture containing 36% L-LA + 36% D-LA + 28% *meso*-LA, plus 0.5 wt % linear oligomers.[15]

In view of the above challenges facing effective utilization of *meso*-LA, we devised a strategy for conversion of *meso*-LA directly into the desired product *it*-PLA by organic catalysts, through a two-step process that can be carried out in a one-pot fashion: epimerization of *meso*-LA to *rac*-LA, followed by stereoselective or enantioselective polymerization (Scheme 1). To realize this strategy, one must first develop an epimerization reaction that can achieve quantitative conversion of *meso*-LA to *rac*-LA and

Scheme 1. Proposed New Strategy for Utilization of *meso*-LA
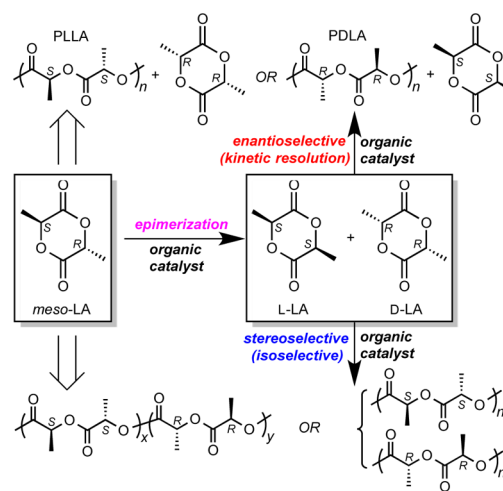
then discover an enantioselective catalyst that can perform the effective kinetic resolution polymerization of *rac*-LA.

To the first task, we reasoned that the dynamic *meso*-LA ⇔ *rac*-LA equilibrium should be controlled by temperature, base, solvent, and solubility difference. For instance, carrying out the epimerization at lower temperatures (e.g., 25 °C or room temperature, RT) should shift the equilibrium further toward *rac*-LA[8] and also avoid any LA oligomerization, and finding conditions that can continuously remove the formed *rac*-LA from the reaction mixture should drive the epimerization to completion. However, an immediate challenge was the epimerization rate at RT is too low to be practical. Indeed, our initial screening of some potent base catalysts such as quinidine (QD), *β*-isoquinidine (*β*-IQD), 1,4-diazabicyclo [2.2.2]octane (DABCO), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for the *meso*-LA epimerization reaction with 2 mol % base at RT rendered no or negligible epimerization after up to 2 days of reaction, or just resulted in polymerization (by DBU). Inspired by the "frustrated Lewis pair" (FLP) chemistry[16] that takes advantage of the unquenched, orthogonal Lewis acid and Lewis base reactivity for FLP-type activation of small molecules or tandem catalysis (FLP- and classical LP working in concert) in polymerization of polar monomers,[17] we turned our attention to investigations into LPs for *meso*-LA epimerization. Just like the above Lewis bases, the Lewis acids such as B(C₆F₅)₃, when used alone, exhibited no activity. Excitingly, when combined together, the LP DABCO/B(C₆F₅)₃ catalyzes rapid, essentially quantitative epimerization of *meso*-LA to *rac*-LA (Figure 1).
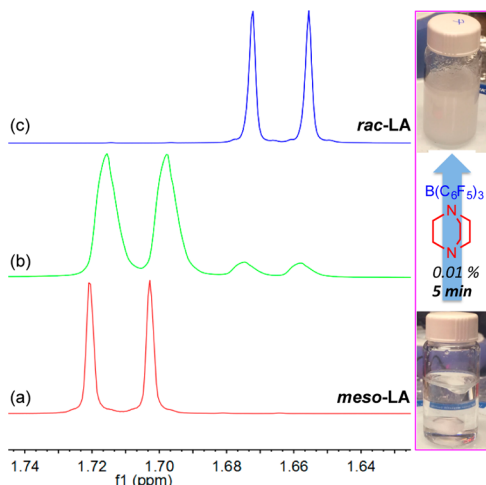

Figure 1. Left: NMR spectra (CDCl₃) of the methyl region of: (a) pure *meso*-LA; (b) *meso*-LA/*rac*-LA (90/10) from NatureWorks; and (c) isolated pure *rac*-LA from epimerization of *meso*-LA. Right: pictorial representation of fast epimerization of *meso*-LA to *rac*-LA (which precipitates out of solution) by DABCO/B(C₆F₅)₃ (2.88 g scale, 2.0 M in toluene, 5 min, 95.4% conversion).

When carried out in CH₂Cl₂ (1.0 M) by DABCO/B(C₆F₅)₃ (2.0 mol %), the *meso*-LA epimerization reaction achieved a maximum *meso*-to-*rac*-LA conversion of 82%. Starting with *rac*-LA under the same conditions, the same mixture of *rac*/*meso* lactides formed in a ratio of ca. 82:18. Variations of acids and bases showed that DABCO/B(C₆F₅)₃ and Et₃N/B(C₆F₅)₃ performed similarly and appeared to give the best conversion (Table S1). Thus, one of these LPs, DABCO/B(C₆F₅)₃, was used for further optimization. Changing the solvent to more polar, donor solvents such as DMF and DMSO drastically

lowered the conversion to ~20% or below. On the other hand, use of the relatively nonpolar toluene, which enabled precipitation of *rac*-LA from solution once formed markedly enhanced the *meso*-to-*rac*-LA conversion to 95%. Increasing the initial [*meso*-LA]₀ concentration from 0.2 M to 0.5, 1.0, 1.5, and 2.0 M resulted in a steady increase in the conversion from 86% to 93, 95, 97, and 98%, respectively (Table S1). While keeping the concentration at 2.0 M, we gradually lowered the LP loading from 2.0 mol % to 1.0, 0.5, 0.2, 0.1, 0.05, 0.01, 0.005, and 0.002 mol % (i.e., 20 ppm) and found the *meso*-to-*rac*-LA conversion still remained at an essentially quantitative level of 97−99%. The epimerization is rapid, as shown by the reaction with 0.01 mol % of the LP, which achieved 95.4% *meso*-to-*rac*-LA conversion in just 5 min (Figure 1). To more accurately assess the rate of the epimerization, the reaction was stopped at different times, and the conversion−time plot gave a very high turnover frequency of 81.8 s⁻¹ or 2.95×10^5 h⁻¹ (Figure S1). The epimerization can also be carried out in bulk at 70 °C, still achieving a high *meso*-to-*rac*-LA conversion of 94−97%, depending on catalyst loading and reaction time (Table S1). At this temperature, precipitation of *rac*-LA from *meso*-LA shifts the equilibrium further toward *rac*-LA. This LP-catalyzed epimerization worked similarly, irrespective of the initial *meso*-LA/*rac*-LA ratio in the feed (Table S1). Isolation of the epimerization product was performed on a 5.76 g scale of the reaction with 20 ppm catalyst loading in toluene at RT; upon completion of the reaction, simple filtration, followed by washing with cold toluene and drying under vacuum, afforded the pure *rac*-LA in 88.2% isolated yield. The filtrate was a mixture of *rac*-LA (95%) and *meso*-LA (5%), which can be reused for the epimerization. Alternatively, the crude epimerization product was purified by flash chromatography on silica gel to give *rac*-LA (>98% purity) in 98.6% yield.

This observed remarkable performance of the LP is presumably due to the cooperativity of the LP in that the [B] Lewis acid activates the substrate *meso*-LA via carbonyl coordination, which accelerates the depronation at the tertiary carbon of the activated substrate by the [N] base (**I**), leading the planar enolate intermediate (**II**) that can be reprotonated causing epimerization. An alternative mechanism that possibly involves reshuffling of the two halves of the lactide by transesterification was excluded as the same mixture of *rac*/*meso* lactides in a ratio of ca. 82:18 was formed when homochiral L-LA was treated under the same epimerization conditions as described above for the *meso*-LA. Noteworthy is that use of the preformed classical Lewis adduct (insoluble) DABCO·B(C₆F₅)₃[18] performed identically to the current standard procedure that premixes the borane with *meso*-LA, followed by addition of DABCO to start the reaction. This result indicates that, under the current catalytic conditions, this adduct can reversibly and rapidly dissociate into the respective base and acid to catalyze the epimerization.
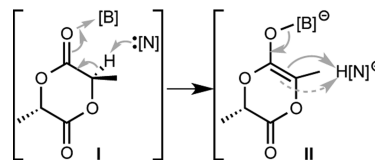
Having achieved the first task of quantitative epimerization of *meso*-LA to *rac*-LA, we tackled the second task of developing an enantioselective catalyst that can perform the effective kinetic resolution polymerization of *rac*-LA. We reasoned that the bifunctional *β*-isocupreidine (*β*-ICD), which represents the first example of organocatalytic enantioselective polymerization of

Table 1. Kinetic Resolution Polymerization of *rac*-LA at 25 °C by Chiral Organic Catalysts[a]

run no.	cat.	solvent (*rac*-LA conc.)	[M]/[Cat]/[I]	time (h)	conv.[b] (%)	ee[c] (%)	k_S/k_R[d] (s)	M_n[e] (kg/mol)	Đ[e] (M_w/M_n)
1	β-ICD	DCM (1.67M)	50/1/1	6	47.6	40	3.8	5.53	1.14
2	CPD	DCM (1.67M)	50/1/1	131	42.4	33	3.6	5.37	1.14
3	**1**	DCM (1.67M)	100/1/1	7	47.8	63	10	11.3	1.13
4	**2**	DCM (1.67M)	50/1/1	36	53.5	25	1.9	6.72	1.10
5	**3**	DCM (1.67M)	50/1/1	22	52.4	−33[f]	0.4	6.88	1.11
6	**4**	DCM (1.67M)	50/1/1	7	50.1	85	32	6.38	1.16
7	**4**	DCM (1.67M)	100/1/1	25	50.2	83	26	10.3	1.14
8	**4**	FB (0.31M)	50/1/1	30	50.8	89	41	6.10	1.12
9	**4**	DFB (0.31M)	50/1/1	17	50.6	**91**	**53**	7.21	1.14
10	**4**	DFB (0.31M)	100/1/1	43	50.5	88	38	11.0	1.12
11[g]	**4**	DFB (0.31M)	100/1/1	40	51.0	88	35	10.4	1.13
12	**5**	DCM (1.67M)	100/1/1	18	49.5	64	8.8	11.0	1.13
13	**6**	DCM (1.67M)	100/1/1	48	51.0	67	9.0	10.9	1.15
14	**7**	DCM (1.67M)	100/1/1	29	48.8	64	9.7	10.0	1.12
15	**8**	DCM (1.67M)	100/1/1	18	49.0	−24[f]	0.5	11.1	1.13

[a]Carried out at 25 °C unless indicated otherwise, using BnOH as initiator (I), in dichloromethane (DCM), toluene (TOL), fluorobenzene (FB), or *o*-difluorobenzene (DFB). [b]Determined by ^{1}H NMR in CDCl$_3$. [c]Enantiomeric excess of the unreacted monomer measured by chiral HPLC. [d]Calculated from $\{\ln[(1 − \text{conv.})(1 − ee)]\}/\{\ln[(1 − \text{conv.})(1 + ee)]\}$. [e]Number-average molecular weight (M_n) and polydispersity index (Đ = M_w/M_n) determined by gel-permeation chromatography (GPC) at 40 °C in DMF relative to poly(methyl methacrylate) (PMMA) standards. [f]L-LA was left. [g]One-pot reaction from *meso*-LA.

rac-LA but with a low stereoselectivity factor ($s = k_S/k_R$ or k_L/k_D) of 4.4 and a low ee value of 45.1% (kinetically resolved D-LA) at 48.4% monomer conversion,[5] could be modified or redesigned into advanced chiral organic catalysts with potentially much higher stereoselectivity. While both β-ICD and cupreidine (CPD) are effective for partial kinetic resolution of *rac*-LA (runs 1 and 2, Table 1), their methylated derivatives β-IQD and QD had no activity for ROP of *rac*-LA, which reveals the phenol OH in β-ICD and CPD is crucial as an H-bonding donor in this bifunctional catalysis. Replacing the OH group in β-ICD with a thiourea group, a double H-bonding donor, furnished catalyst **1** (Figure 2),[19] which significantly enhanced not only the ROP
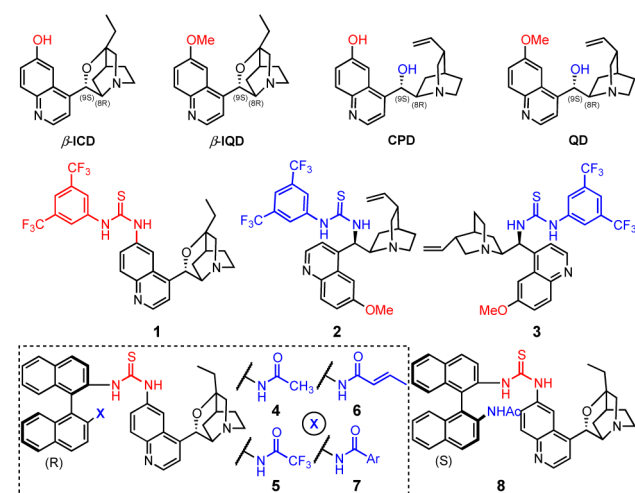

Figure 2. Structures of chiral organic catalysts used for kinetic resolution polymerization of *rac*-LA in this study.

activity but also the stereoselectivity with $s = 10$ and ee = 63% at 47.8% conversion in dichloromethane (run 3). Substituting the OH group in QD and quinine (QN) with the thiourea group gave the corresponding pseudoenantiomers **2** and **3**;[20] although this substitution turned on the ROP activity of the inactive QD

and QN precursors, the stereoselectivity of **2** and **3** (runs 4 and 5) was much inferior to **1**, β-ICD, or CPD.

The observed much improved activity and stereoselectivity by **1** pointed us in the right direction for developing better catalysts based on derivatizing β-ICD. To this end, we reasoned that introduction of a chiral double H-bonding donor based on the binaphthyl-amine (BINAM) framework should exert double stereodifferentiation due to asymmetric activation of both the monomer (by the chiral acid) and the propagating P−OH species (by the chiral amine). It has recently been reported that a BINOL-based phosphoric acid achieved a high s factor of $k_D/k_L =$ 28 at 49% monomer conversion.[6] Accordingly, we designed and synthesized new catalyst **4**, which combines three essential elements (β-ICD core, thiourea functionality, and BINAM) into a single molecule. Indeed, **4** exhibited drastically enhanced the stereoselectivity over catalyst **1**, now achieving a high s factor of 32 and 85% ee at 50.1% monomer conversion (run 6). Lowering the catalyst loading from 2 to 1 mol % increased the PLA M_n to $1.03 × 10^4$ g/mol (Đ = 1.14, run 7) while maintaining similar stereoselectivity. Optimization of the reaction by using fluorobenzene as the solvent further enhanced the s factor to 41 and the ee value to 89% at 50.8% monomer conversion (run 8). When *o*-difluorobenzene (DFB) was used, the s factor reached the highest of 53 and the ee value of 91% at 50.6% monomer conversion (run 9). Changing the X group on the BINAM from −NHAc (**4**) to −NHCOCF$_3$ (**5**), −NHCOCH═ CHMe (**6**), and −NHCOAr (**7**, Ar = 4-CF$_3$C$_6$H$_4$) drastically reduced catalyst stereoselectivity (runs 12−14). Flipping the BINAM from R to S (**8**) yielded a much inferior catalyst (run 15).

With both tasks now having been met, we set out to examine the possibility of carrying out *meso*-LA to *rac*-LA epimerization and enantioselective polymerization in a one-pot fashion. We first confirmed that the isolated *rac*-LA from the epimerization reaction was polymerized into *it*-PLA (P_m = 0.94, at −75 °C, Figure 3), the result of which is nearly identical to the ROP of *rac*-LA (P_m = 0.95, at −75 °C, or P_m = 0.72, at 20 °C) reported in the literature,[4a] using the same catalyst phosphazene ^{t}Bu-P$_2$. In comparison, the chiral catalyst **4** produced *it*-PLA with a higher P_m value of 0.82 at 25 °C (the ee of the unreacted monomer was
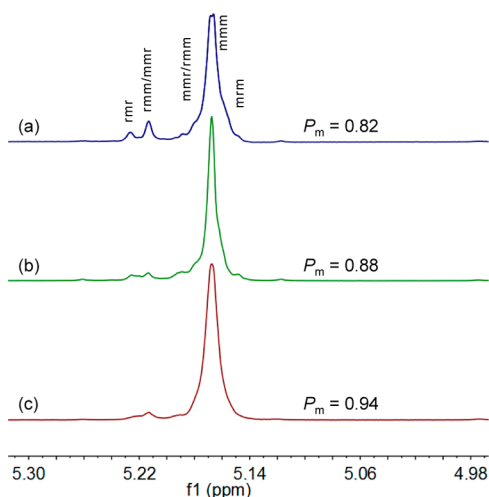
Figure 3. Homonuclear decoupled ^1H NMR spectra (400 MHz, $CDCl_3$) of the methane region of PLAs from *rac*-LA: (a) catalyst **4**, 25 °C, 82.9% conversion; (b) catalyst **4**, 25 °C, 50.5% conversion; (c) ^tBu-P_2, −75 °C, >99% conversion.

99%). Finally, we first performed the quantitative epimerization of *meso*-LA (0.721 g) by DABCO/B($C_6F_5)_3$ (0.01 mol %) in toluene, removed the solvent to give *rac*-LA/*meso*-LA in a ratio of 99/1, and then added catalyst **4** in DFB for subsequent kinetic resolution polymerization. The results were similar (only with a slightly lower *s* value, run 11 vs 10) to those obtained using the pure *rac*-LA under the same reaction conditions.

In conclusion, we have discovered that the Lewis pair DABCO/B($C_6F_5)_3$ catalyzes rapid and quantitative epimerization of *meso*-LA, often regarded as a "waste" side-product of the L-LA production process, into *rac*-LA. The keys for achieving quantitative conversion of this isomerization process include (a) a highly effective LP catalyst system that enables the rapid epimerization at ambient temperature, under which conditions the equilibrium is shifted further toward *rac*-LA and LA oligomerization can also be avoided and (b) continuous removal of the formed *rac*-LA from the reaction mixture through precipitation of *rac*-LA from solution due to solubility differences. This epimerization method can convert LA stereoisomers in any ratio into essentially pure *rac*-LA. We also developed a highly enantioselective bifunctional chiral organic catalyst. Using this catalyst, *rac*-LA is polymerized enantioselectively into *it*-PLLA and optically resolved D-LA with a high stereoselectivity factor of 53 and the ee value of 91% at 50.6% monomer conversion. The epimerization and kinetic resolution polymerization can be coupled into a one-pot process, effectively transforming *meso*-LA directly into *it*-PLLA and D-LA.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08658.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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