solid (96% *ee*). M.p. 114 °C; $[\alpha]_D^{25} = -46.9°$ ($c = 1.00$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1674\ cm^{-1}$ (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz): $\delta = 1.23$ (3H, t, $J = 7.6$ Hz, Me), 2.15 (3H, s, Me), 2.39 (3H, s, Me), 2.54 (2H, q, $J = 7.6$ Hz, CH_2), 5.20 (1H, d, $J = 6.1$ Hz, NH), 5.51 (1H, d, $J = 8.4$ Hz, CH), 6.09 (2H, s), 6.97 (2H, d, $J = 6.1$ Hz, Ar), 6.98 (2H, $J = 6.1$ Hz, Ar), 7.21 (2H, d, $J = 8.4$ Hz, Ar), 7.63 ppm (2H, d, $J = 8.4$ Hz); MS (EI): *m/z* (%): 358 [$M^+ - 1$] (0.5), 288 [$M^+ - 69$] (5.6), 202 [$M^+ - 155$] (100); Elemental analysis (%) calcd for $C_{20}H_{23}NO_3S$: C 67.20, H 6.49, N 3.92; found: C 67.04, H 6.42, N 3.74.

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[6] CCDC-167239 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Crystal data of **1e**: $C_{18}H_{18}ClNO_3S$; $M_r = 363.84$; $T = 293(2)$ K; monoclinic, space group $P2(1)$; $a = 8.513(3)$, $b = 12.076(4)$, $c = 9.767(3)$ Å, $\beta = 112.259(6)°$, $V = 929.3(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.300\ Mg\,m^{-3}$; $F_{000} = 380$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0475$l, $R_2 = 0.0833$.

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[(salen)Al]-Mediated, Controlled and Stereoselective Ring-Opening Polymerization of Lactide in Solution and without Solvent: Synthesis of Highly Isotactic Polylactide Stereocopolymers from Racemic D,L-Lactide

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Polylactides (PLAs) are among the most important synthetic biodegradable polymers investigated for biomedical and pharmaceutical applications such as controlled drug delivery, resorbable sutures, medical implants, and scaffolds for tissue engineering.[1] On the basis of annually renewable resources such as corn and sugar beets, PLAs are also promising degradable substitutes for petrochemical-based polyolefins.[2] The physical, mechanical, and degradation properties of PLAs are intimately dependent on the chain stereochemistry. For instance, isotactic poly(L-LA) (LA = lactide), a highly crystalline material with a $T_m \approx 170\,°C$, has excellent mechanical properties and degrades rather slowly, whereas atactic poly(D,L-LA) is amorphous and subject to a relatively fast degradation. Stereocontrol, therefore, is crucial in the synthesis of polylactides. Most catalysts, including stannous octoate, zinc lactate, and aluminum alkoxides, do not bias towards different enantiomers in the ring-opening polymerization of D,L-lactide, thereby furnishing PLAs with randomly distributed stereocenters.[3] Recently it was reported that a few single-site lactide-polymerization catalysts did show stereoselectivity. For example, [(bdi)ZnO*i*Pr] (bdi = β-diiminate) polymerized D,L-LA in such a way as to afford a heterotactic PLA, and chiral tris(pyrazolyl)borate magnesium complexes preferentially polymerized *meso*-LA in the presence of a mixture of *meso*-LA and D,L-LA (diastereoselectivity).[4]

It has long been a challenge to prepare PLAs with long isotactic sequences out of D,L-LA through isospecific polymerization (Scheme 1), since these stereoblock copolylactides are expected to be hard and strong as highly crystalline poly(L-LA)s but with varying degrees of crystallinity and degradation rates, depending on the average length of the isotactic blocks. So far, examples of isospecific lactide polymerization are limited to Schiff base aluminum alkoxide catalysts in CH_2Cl_2 or in toluene,[5] in which the binaphthyl Schiff base ligands impose the best stereochemical as well as molecular-weight control. However, the synthesis of the binaphthyl Schiff base ligand is time-consuming. Besides, solution polymerization with these catalysts is not a practically viable process. The following requirements must be satisfied for a catalyst to be industrially attractive:

1) The starting organic ligands should be commercially available and inexpensive.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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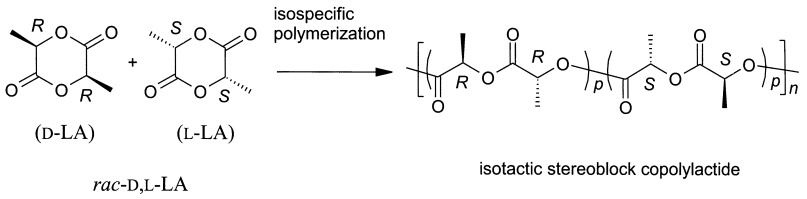


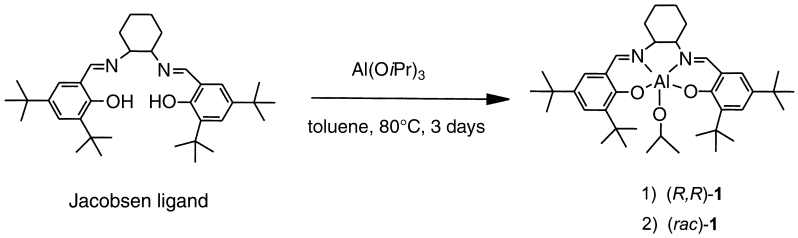
Scheme 1. Isospecific polymerization of D,L-LA to isotactic stereoblock copolylactides.

2) The synthesis of the catalyst must be straightforward and high-yielding.
3) The polymerization should preferably be conducted in the absence of solvents, which implies that a high temperature of at least 130 °C is required for the solvent-free polymerization of D,L-LA. Therefore the catalyst has to be sufficiently stable at the polymerization temperature.
4) Polymers with a controlled M_n and low polydispersity should be obtained in high yield.
5) Ideally, new polymers with distinct microstructures as well as useful properties should be prepared from inexpensive substrates.

Herein, we report the synthesis of new salen aluminum alkoxides (both enantiopure and racemic) by employing the Jacobsen ligand, an inexpensive commercial starting material with demonstrated usefulness in various asymmetric reactions, for example, asymmetric olefin epoxidation, asymmetric epoxide-ring-opening reactions, hydrolytic kinetic resolution of terminal epoxides.[6] Most notably, these catalysts provide high isospecificity and excellent control in both solution and solvent-free polymerization of lactide at elevated temperatures. To the best of our knowledge, this is the first example of solvent-free stereoselective lactide polymerization.

Both (*R,R*)-**1** and *rac*-**1** were obtained in high yields by the reaction of *R,R* or *rac* Jacobsen ligand with aluminum triisopropoxide in toluene (Scheme 2). The ^{27}Al NMR spectrum of (*R,R*)-**1** in [D_8]toluene/toluene (*v*/*v* 1:2) solvent had only a single resonance at $\delta = 35.45$ ppm ($w_{1/2} = 954$ Hz), which supports a five-coordinate state for Al.[7]

Initial experiments conducted in toluene at 70 °C ($[M]_0/[I]_0 = 62{:}1$, $[M]_0 = 0.8$ mol L^{-1}) revealed that both (*R,R*)-**1** and (*rac*)-**1** yielded PLAs with a well-controlled M_n and a very low polydispersity index (M_w/M_n) (Table 1, entries 1–3, 6–7). End-group analysis by NMR spectroscopy and MALDI-TOF mass spectroscopy showed that the polymer chains were systematically end-capped with an isopropyl ester and a hydroxy group, respectively. A steady evolution of M_n, while retaining a low M_w/M_n over the course of polymerization, was evidenced by gel-permeation chromatography (GPC) (Figure 1). Transesterification was practically absent, even after a long polymerization time, as revealed by



Scheme 2. Preparation of (*R,R*)-**1** and (*rac*)-**1** from the Jacobsen ligand.

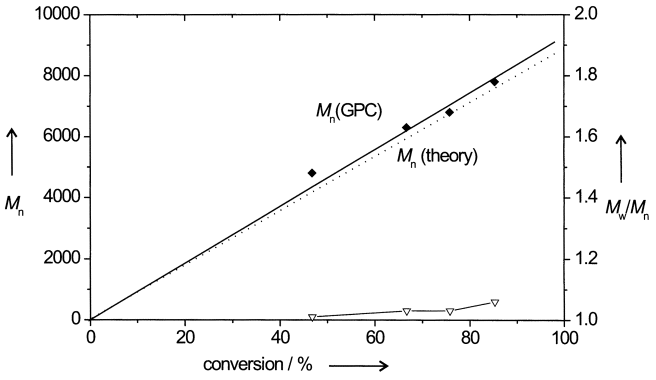


Figure 1. Dependence of M_n and polydispersity index (M_w/M_n) of polylactide on monomer conversion using (*rac*)-**1** for D,L-LA polymerization in toluene at 70 °C. $[M]_0/[I]_0 = 62/1$. ◆: M_n (GPC), ▽ : M_w/M_n, ····: M_n (theory).

Table 1. Ring-opening polymerization of lactide mediated by (*R,R*)-**1** or (*rac*)-**1**.

Entry	Catalyst	Monomer	M/I	*T* [°C]	*t* [d]	Conversion [%]	$M_n \times 10^{-3}$ NMR[a]	$M_n \times 10^{-3}$ GPC[b]	$M_n \times 10^{-3}$ Theo.[c]	M_w/M_n GPC[b]	P_i[d]
1		L-LA	62	70	4	97.0	9.6	9.9	8.7	1.05	–
2a		D,L-LA	62	70	2	21.1	2.5	2.4[f]	1.9	1.04[f]	0.92
2b	(*R,R*)-**1**	D,L-LA	62	70	4	36.3	3.5	3.3[f]	3.2	1.04[f]	–
3		D,L-LA	62	70	24	87.8	8.4	8.5	7.8	1.08	–
4		D,L-LA	100	110	6	94.0	13.9	13.7	13.5	1.31	–
5[e]		D,L-LA	200	130	2	86.4	23.7	21.6	24.7	1.18	–
6		L-LA	62	70	5.1	93.1	7.4	8.6	8.1	1.09	–
7	(*rac*)-**1**	D,L-LA	62	70	12	85.3	8.5	7.7	7.6	1.06	0.93
8[e]		D,L-LA	200	130	2	94.8	20.3	24.9	27.3	1.37	0.88

[a] Obtained by ^{1}H NMR spectroscopic end-group analysis. [b] Determined by gel-permeation chromatography (GPC) in $CHCl_3$, universal calibration relative to polystyrene standard. [c] Calculated based on monomer/initiator ratio and conversion. [d] The parameter P_i is the probability of forming a new *i*-dyad. On the basis of enantiomorphic site control statistics, the tetrad proportions of PLAs obtained from D,L-LA polymerization in terms of P_i can be expressed as follows: $[iii] = [P_i^2 + (1-P_i)^2 + P_i^3 + (1-P_i)^3]/2$, $[isi] = [P_i(1-P_i) + P_i(1-P_i)^2]/2$, $[iis] = [sii] = [sis] = [P_i^2(1-P_i) + P_i(1-P_i)^2]/2$, where *i* denotes isotactic and *s* syndiotactic.[5g] [e] Solvent-free polymerization conducted at 130 °C. [f] Determined by MALDI-TOF mass spectrometry.

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the MALDI-TOF mass spectrum (see Supporting Information). This is in sharp contrast with the results reported for achiral [2,2′-{ethylenebis(nitrilomethylidine)}diphenolate]aluminum methoxides, which promoted significant ester-exchange reactions under similar conditions.[8] Therefore, it is clear that the polymerization is a perfectly living process, and the polymerization involves acyl-oxygen cleavage of lactide monomer and insertion into aluminum–alkoxide bonds.

Most remarkably, in all cases a crystalline PLA was isolated, suggesting that long isotactic sequences are generated during D,L-LA polymerization. Detailed microstructural analysis by using ^{13}C NMR spectroscopy corroborated the high isotacticity of the PLAs. The carbonyl as well as the methine carbon regions of the ^{13}C NMR spectrum of the PLA obtained by polymerizing D,L-LA with (*rac*)-**1** are shown in Figure 2. Resonances in terms of tetrad or hexad sensitivity were

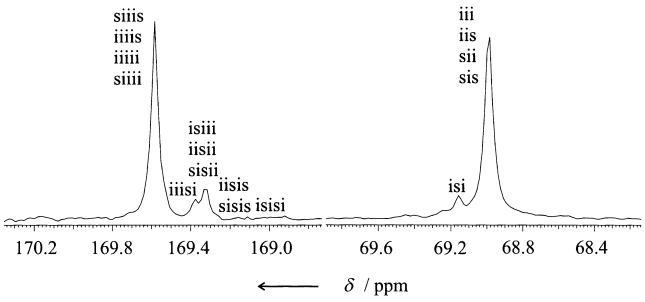

Figure 2. ^{13}C NMR spectrum (75.26 MHz, $CDCl_3$) showing hexad and tetrad probabilities of PLA prepared by polymerizing D,L-LA using (*rac*)-**1** ($[M]_0/[I]_0 = 62/1$, $[M]_0 = 0.8$ mol L^{-1}, toluene, 70 °C, 12 days, 85.3 % conversion).

assigned according to Kasperczyk and Vert and co-workers.[9] The degree of stereoselectivity, which may be defined by the parameter P_i (the probability of forming a new *i*-dyad), can be determined from the relative tetrad intensities.[5g] According to enantiomorphic-site-control statistics, a P_i value of 0.93 is obtained for (*rac*)-**1**-initiated D,L-LA polymerization (Table 1, entry 7). The high isotacticity was further confirmed by the high intensity of the *iii*-resonance in the methine region of the homonuclear decoupled ^1H NMR spectrum (see Supporting Information).[10] In addition, differential scanning calorimetry (DSC) revealed that this polymer had a high T_m of 183.5 °C ($\Delta H_{fus} = 41.3$ J g^{-1}), which is significantly higher than that of the optically pure poly(L-LA) ($T_m = 168.4$ °C, see Supporting Information).[11] These results are very close to those reported for the PLAs prepared by the polymerization of D,L-LA using racemic binaphthyl Schiff base aluminum catalysts.[5e–g] Based on the microstructural data and thermal characteristics, we conclude that isotactic stereoblock copolylactides are the most likely structures.

Under identical polymerization conditions, the polymerization of D,L-LA with enantiopure catalyst (*R,R*)-**1** afforded polymers with high isotacticity at low conversion, but decreased isotacticity at higher conversion. The P_i based on a PLA sample acquired at 21.1 % conversion is 0.92 (Table 1, entry 2a), which is close to the stereoselectivity observed for D,L-LA polymerization with (*rac*)-**1** at high conversion. Kinetic studies revealed that (*R,R*)-**1** polymerized L-LA significantly faster than did the D-enantiomer, with a relative polymerization rate $k_{rel} = k_{L\text{-}LA}/k_{D\text{-}LA} = \sim 14$. The gradually increasing relative concentration of the D-LA isomer in the monomer pool as the "selected" L-LA is converted into PLA during the polymerization process is responsible for the decreasing isotacticity at high conversion. The PLA thus obtained has a gradient stereosequence changing from long isotactic L-lactyl units to long isotactic D-lactyl units. Similar results were reported for D,L-LA polymerization with a (*R,R*)-binaphthyl Schiff base complex of aluminum, but it should be emphasized that contrary to (*R,R*)-**1**, (*R*)-binaphthyl Schiff base aluminum methoxide preferentially polymerizes D-LA.[5d] All these observations indicate that the Jacobsen ligand imposes stereochemical control that is comparable with binaphthyl Schiff base in toluene at 70 °C and that a site-control mechanism is operative in the stereoselection process.

Polymerization at higher temperatures was carried out to investigate the influence of reaction temperature on the polymerization rate and stereoselectivity. D,L-LA polymerization in toluene at 110 °C with (*R,R*)-**1** proceeded much faster than polymerization at 70 °C, and, most importantly, a crystalline polymer with a controlled M_n resulted (Table 1, entry 4). The high level of stereoselectivity maintained at elevated temperatures encouraged us to carry out solvent-free polymerization. Interestingly, excellent molar-mass control as well as stereochemical control was observed, even when D,L-LA was polymerized in the absence of solvent at 130 °C (Table 1, entries 5 and 8). At a monomer/initiator molar ratio of 200, high conversions were obtained within 2 days, providing polymers of rather low polydispersity ($M_w/M_n = 1.18$ for (*R,R*)-**1**, 1.37 for (*rac*)-**1**). Microstructural analysis showed that both polymers contain long isotactic sequences. (*R,R*)-**1** furnished an amorphous polylactide, whereas (*rac*)-**1** afforded a hard crystalline polymer. A P_i value of 0.88 was determined for D,L-LA polymerization in the presence of (*rac*)-**1** (Table 1, entry 8). These results are extraordinary, since no other catalyst reported thus far is able to effect such a high stereoselectivity in lactide polymerization under these polymerization conditions (110 °C in toluene or in the absence of solvent at 130 °C).

In summary, we have demonstrated that new [(salen)Al] catalysts, either in solution or in the absence of solvent, exert excellent molecular-weight control as well as stereochemical control in lactide polymerization. Polylactides with varying isotactic lengths, which affords either a crystalline or amorphous polymer, can be prepared directly from racemic D,L-lactide. Additionally, selective polymerization of L-LA in the presence of D,L-lactide imposed by (*R,R*)-**1** might provide a novel and efficient pathway to optically pure D-lactide monomer. Kinetic and mechanistic studies as well as new polymer syntheses are underway.

Experimental Section

General: All experiments were carried out under argon using Schlenk techniques or under nitrogen in a glovebox. Solvents were thoroughly dried prior to use.

(*R,R*)-**1**: Aluminum isopropoxide (0.583 g, 2.85 mmol), *R,R* Jacobsen ligand (1.56 g, 2.85 mmol), and toluene (15 mL) were added to a dried

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reaction vessel equipped with a magnetic stirrer bar. After the mixture was stirred for 3 days at 80 °C, the solvent and volatile components were removed in vacuo. The yellow solid was then washed with hexane, filtered, and dried in vacuo. Yield: 95.6 %. Elemental analysis: calcd: C 74.25, H 9.43, N 4.44, Al 4.27; found: C 73.94, H 9.53, N 4.52, Al 4.24; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.36$ (s, 1H), 8.15 (s, 1H), 7.47–7.50 (dd, $J = 2.7$, 8.0 Hz, 2H), 6.98–7.05 (dd, $J = 2.7$, 17.0 Hz, 2H), 3.92 (t, $J = 9.6$ Hz, 1H), 3.71 (sept, $J = 5.7$ Hz, 1H), 3.04 (t, J 9.6 Hz, 1H), 2.60 (br s, 1H), 2.40 (br s, 1H), 2.06 (b, 2H), 1.55 (s, 9H), 1.52 (s, 9H), 1.47 (m, 4H), 1.30 (s, 9H), 1.29 (s, 9H), 0.86 ppm (dd, $J = 5.7$, 7.5 Hz, 6H); ^{27}Al NMR (104 MHz, toluene/[D_8]toluene (v/v: 2/1), $Al_2(SO_4)_3$ in D_2O): $\delta = 35.45$ ppm ($w_{1/2} = 954$ Hz). (*rac*)-**1**: Elemental analysis: calcd: C 74.25, H 9.43, N 4.44, Al 4.27; found: C 74.28, H 9.42, N 4.50, Al 4.13; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.36$ (s, 1H), 8.15 (s, 1H), 7.47–7.50 (dd, $J = 2.4$, 7.5 Hz, 2H), 6.98–7.05 (dd, $J = 3.0$, 17.1 Hz, 2H), 3.92 (t, $J = 10.5$ Hz, 1H), 3.71 (sept, $J = 5.7$ Hz, 1H), 3.04 (t, $J = 10.5$ Hz, 1H), 2.60 (br s, 1H), 2.40 (br s, 1H), 2.06 (br s, 2H), 1.55 (s, 9H), 1.52 (s, 9H), 1.47 (m, 4H), 1.30 (s, 9H), 1.29 (s, 9H), 0.86 ppm (dd, $J =$ 5.7, 7.5 Hz, 6H).

Solution polymerization (typical experiment): The catalyst (*rac*)-**1** (0.102 g, 0.162 mmol), D,L-LA (1.44 g, 10 mmol), and toluene (12 mL) were added to a dried reaction vessel equipped with a magnetic stirrer bar. The vessel was placed in an oil bath at 70 °C (thermostat control) and stirred for 12 days. Acetic acid was added to terminate the polymerization. A sample was taken for the determination of the conversion by ^{1}H NMR spectroscopy. The solvent was removed by rotary evaporation, the remaining residues were redissolved in CH_2Cl_2, and the polymer was precipitated from excess cold methanol. Filtration, followed by drying at 40 °C in vacuo yielded a white crystalline polymer. Conversion = 85.3 %, M_n (GPC) = 7.7×10^3, $M_w/M_n = 1.06$.

Solvent-free polymerization (typical experiment): The catalyst (*rac*)-**1** (0.065 g, 0.103 mmol) and D,L-LA (3.0 g, 20.8 mmol) were stirred at 130 °C for 2 days. A sample was taken for determination of the conversion by ^{1}H NMR spectroscopy. The polymer was isolated by dissolution in CH_2Cl_2, precipitation from excess ethanol, filtration, and drying at 40 °C in vacuo. Conversion = 94.8 %, M_n (GPC) = 24.9×10^3, $M_w/M_n = 1.37$.

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Unprecedented Coupling of Allenylidene and Diynyl Metal Complexes: A Bimetallic Ruthenium System with a C_7 Conjugated Bridge**

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Organometallic complexes with π-conjugated bridges have gained importance in view of potential applications in the emerging field of molecular-scale electronic devices.[1,2] An attractive pursuit in this area is the design of molecular wire precursors that allow exchange of electrons through bridges between remote terminal groups.[2–6] A variety of different approaches have been applied to construct such entities, the majority of which have contained an even number of carbon atoms in the bridge.[2,3] By contrast, only a few complexes with

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