Polymerization (VIP)

Highly Heteroselective Ring-Opening Polymerization of *rac*-Lactide Initiated by Bis(phenolato)scandium Complexes**

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Currently there is considerable interest in the controlled ring-opening polymerization (ROP) of lactides (LAs) by well-defined metal initiators because of the biodegradable and biocompatible nature of polylactides (PLAs) and their potentially wide-ranging commercial applications.[1,2] Particularly interesting is that some discrete metal complexes initiate the ROP of *rac*-LA or *meso*-LA in a stereoselective manner,[3–9] and thus PLAs with a variety of architectures ranging from isotactic,[3d–i] syndiotactic,[5] to heterotactic[6–8] can be obtained. Enantiomerically pure or racemic aluminum complexes with chiral salen-type ligands (salen = *N,N'*-bis-(salicylidene)ethylenediamine) were reported to polymerize *rac*-LA to form isotactic or stereoblock/stereogradient PLA,[3a–g] and to polymerize *meso*-LA to form syndiotactic PLA through enantiomorphic site control.[5a] Achiral aluminum–salen or salan complexes (salan = *N,N'*-bis(*ortho*-hydroxybenzyl)ethylenediamine) produce isotactic or heterotactic PLA from *rac*-LA through a chain-end control mechanism.[3h,i,6] Magnesium,[7b,d] zinc,[7c,d] calcium,[7d,e] and yttrium[8] complexes are highly active for ROP of *rac*-LA, in some cases showing significant preference for heterotactic dyad enchainment. Despite considerable efforts devoted to initiator design,[3–10] factors governing stereocontrol during the ROP of lactides are still not well understood. Herein we report that a series of scandium complexes with 1,ω-dithia-alkanediyl-bridged bisphenolato (OSSO)-type ligands (Table 1) show high heterotactic selectivity during the ROP of *rac*-LA. This selectivity involves a new type of dynamic monomer recognition based on the fluxionality of the ancillary ligand. Group 3 complexes with such ligands have previously been found to be active initiators for ROP of L-LA,[11a,b] and a slight heterotactic preference during the ROP

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Table 1: Scandium complexes **1–7**.

Bridge	-∩-	R[1]	R[2]	OSSO	Complex
C₂	-(CH₂)₂-	*t*Bu	Me	etbmp	**1**
	-(CH₂)₂-	cumyl	cumyl	etccp	**2**
		*t*Bu	Me	cytbmp	**3**
C₃	-(CH₂)₃-	*t*Bu	Me	ptbmp	**4**
C₄		*t*Bu	Me	xytbmp	**5, 5a**
		1-ada[a]	Me	xytamp	**6**
		*t*Bu	Me	cmtbmp	**7**

[a] ada = adamantyl.

of *rac*-LA has been noted for the corresponding aluminum complexes.[11c]

As was reported for scandium complexes **1** and **4**,[11a] the derivatives **2**, **3**, and **5–7** (Table 1) were readily synthesized by using the amine elimination reaction of [Sc{N(SiHMe₂)₂}₃-(thf)] with the corresponding bridged bisphenol in toluene at 50–60 °C. Chiral bisphenols cytbmpH₂ and cmtbmpH₂ were used as racemates. With the sterically bulkier bisphenols xytbmpH₂ and xytampH₂, complexes **5a** and **6** were isolated free of the thf ligand. Complexes **2** and **3** with a C₂ bridge show C_1 symmetry in solution (¹H NMR, C₆D₆), whereas the other scandium complexes with longer bridges show C_2 or C_s symmetry as a result of fluxional behavior, similar to findings previously observed.[11a] The monomeric nature of both complexes, which include a distorted octahedral geometry around the scandium center, was confirmed by single-crystal X-ray crystallographic analysis of **5** and **7** (see the Supporting Information).

As shown in Table 2, the scandium complexes **1–7** with bisphenolato ligands were moderately active for the polymerization of *rac*-LA at ambient temperature in THF. Complexes **1–7** displayed almost the same level of activity.

The microstructural analysis[7b,12] of PLAs formed from *rac*-LA with complexes **1–7** revealed that the structure of the complex exerts a significant influence on the tacticity of the growing polymer chain (Table 2). All the scandium complexes showed substantial heterotactic selectivity, with a maximum P_r value of 0.96 observed for complex **4**. The heterotactic selectivity of scandium complexes **1–4** improved as the size of the bisphenolato ligand increased. As recently pointed out by Carpentier and co-workers,[8b] bulky and conformationally flexible *ortho* substituents enhanced the heteroselectivity. However, the influence of the bridge turned out to be most significant. For example, the introduction of one additional

Table 2: ROP of *rac*-lactide initiated by complexes 1–7.[a]

Cat.	$[i\text{PrOH}]_0$/$[\text{Sc}]_0$	t [h]	Conv.[c] [%]	M_{calcd}[d] (×10^4)	M_n[e] (×10^4)	M_w/M_n[e]	P_r[f]
1	–	9	82	3.55	17.8	1.89	0.78
2	–	8	85	3.68	25.9	1.66	0.80
3	–	9	79	3.42	23.8	1.88	0.82
4	–	8	81	3.50	12.6	1.85	0.95
5	–	21	89	3.85	14.3	1.88	0.94
6	–	8	84	3.63	9.30	1.84	0.93
7	–	5	75	3.25	28.5	1.60	0.94
4	1:1	8	63	2.72	5.38	1.55	0.96
4	2:1	8	59	1.28	1.88	1.15	0.94
4	3:1	8	40	0.58	1.09	1.12	0.90
4	3:1	96	93	1.34	1.83	1.06	0.86
5	1:1	5	71	3.07	4.73	1.29	0.94
5	1:1[b]	72	83	3.59	4.42	1.12	0.67

[a] $[\text{LA}]_0/[\text{Sc}]_0 = 300$, $[\text{Sc}] = 2.9$ mmol L^{-1}, THF, 25 °C. [b] In toluene.
[c] Determined by ^{1}H NMR spectroscopy. [d] $M_{\text{calcd}} = (300 \times \%\text{conv.} \times 144.13)/m$, where $m = 1$ (without alcohol) and $m = [i\text{PrOH}]_0/[\text{Sc}]_0$ (with alcohol). [e] Determined by GPC. [f] The probability of forming a new *r* dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy.

carbon atom into the bridge resulted in a surge of hetero-tacticity, with the P_r value increasing from 0.78 for complex **1** to 0.95 for complex **4**; whereas the variation of the *ortho* substituent from *tert*-butyl to 1-methyl-1-phenylethyl (cumyl) led to only a slight improvement ($P_r = 0.80$). The chirality of the ligand skeleton in complexes **3** and **7** did not influence the tacticity, which suggests an absence of enantiomorphic site control during the ROP of *rac*-LA by these scandium complexes.

The addition of excess alcohol to similar initiators was previously found to result in the living polymerization of L-LA.[11b] When *rac*-LA was polymerized with **4** or **5** in the presence of 2-propanol in THF, the number-average molecular weights and the molecular-weight distributions of the resulting PLAs decreased significantly, thereby indicating a more-controlled polymerization. Changing the initiating group from silyl amido to isopropoxide had no influence on the heterotacticity of the PLAs.[8b] The heterotactic selectivity of complexes **4** and **5** was maintained, with P_r values as high as 0.96, which decreased slightly when more than one equivalent of 2-propanol was added. Longer polymerization times also caused some loss of the stereoselectivity because of trans-esterification reactions.[11b] The use of toluene as the solvent led to a dramatic decrease in the heterotacticity from 0.96 to 0.67, thus indicating that the use of THF as the solvent is crucial for the high heterotactic selectivity; a similar effect has been reported for the well-defined Zn, Ca, and Y systems.[7c,d,8b]

To understand the origin of the high heteroselectivity, complex **5** was treated with (*R*)-*tert*-butyl lactate to give complex **8** as a single diastereomer (Scheme 1), which possesses a dimeric structure in the solid state according to results of an X-ray diffraction study (Figure 1).[13] ^{1}H NMR spectroscopic analysis (C$_6$D$_6$) of the crude mixture from the reaction of **5** with (*R*)-*tert*-butyl lactate showed that complex **8** with a Λ,Λ configuration was detected as almost the only product (ca. 95 %).[14b] As depicted in Figure 1, the linear
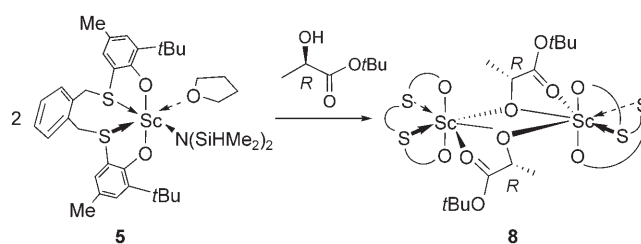
Scheme 1. Synthesis of the dimeric complex **8** with a Λ,Λ configuration.
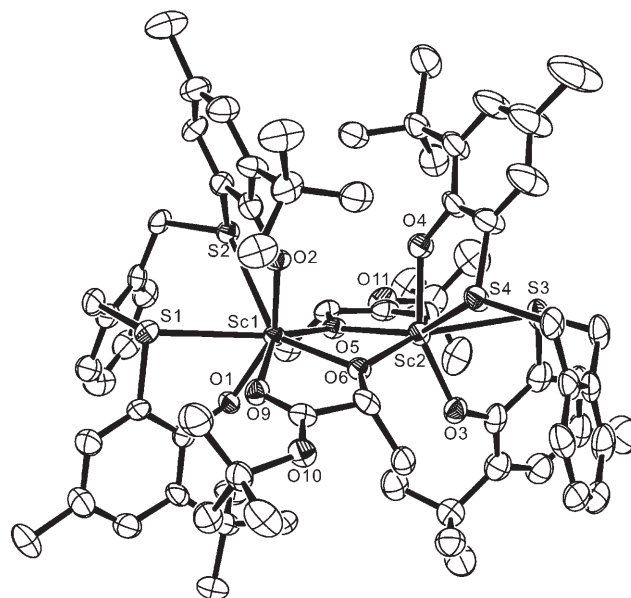

Figure 1. Molecular structure of **8** (with hydrogen atoms omitted) at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Sc1–O1 2.019(4), Sc1–O2 1.983(4), Sc1–O5 2.098(4), Sc1–O6 2.129(4), Sc1–O9 2.254(4), Sc1–S1 2.930(2), Sc1–S2 2.9501(19), Sc2–O3 2.039(5), Sc2–O4 2.006(5), Sc2–O5 2.126(4), Sc2–S3 2.862(2), Sc2–S4 2.931(2); O1-Sc1-O2 151.06(19), S1-Sc1-S2 76.01(5), O1-Sc1-S1 69.35(13), O2-Sc1-S2 65.74(12), S1-Sc1-O5 146.66(12), S2-Sc1-O5 79.59(12), O5-Sc1-O6 72.03(16), O5-Sc1-O9 140.74(16), O3-Sc2-O4 153.2(2), S3-Sc2-S4 76.34(6).

OSSO-type ligands wrap around both scandium centers in **8** with a Λ configuration.[14a] It is evident that for each scandium center, the "upper" *tert*-butyl group of the bisphenolato ligand is located above the Sc-O-C-C-O chelate ring, whereas the α-methyl group of the (*R*)-*tert*-butyl lactate points to the "lower" side. The "lower" *tert*-butyl group is turned away from this methyl group, with a short contact of 2.62 Å between them still being observed. Complex **8** shows a dimeric structure with C_2 symmetry in solution according to its ^{1}H NMR spectra (C$_6$D$_6$, [D$_8$]THF). The addition of [D$_8$]THF to a solution of C$_6$D$_6$ did not lead to any change in the chemical shifts. Although a monomeric species cannot be excluded from the ^{1}H NMR spectroscopic data, by taking the solid structure into account, the dimeric structure of complex **8** is most likely retained in solution. The two subunits of a single bisphenolato ligand are chemically inequivalent: four doublets are displayed for the SCH$_2$ protons of a single ligand up to 95 °C (^{1}H NMR, [D$_8$]toluene), thus indicating a rigid

conformation of the ligand around each metal center. From the fluxional behavior of complex **5** in solution, it is therefore reasonable to assume that the *R* configuration of the lactate ester has selectively induced the *Λ* conformation of the OSSO ligand in complex **8** because of steric repulsion. Taking into account the similarity of the lactate ester and a ring-opened lactide monomer, the same effect can be assumed to be operative during the polymerization of *rac*-LA.

When complex **8**, generated in situ in [D$_8$]THF, was used for the ROP of *rac*-LA, a highly heterotactic PLA was obtained ($P_r = 0.93$). The M_n value was significantly larger than the theoretical value, probably because the cleavage process of the dimer by the lactide monomer was slow, as has been previously reported.[11b] Based on this evidence, we propose the mechanism shown in Scheme 2 for the stereo-
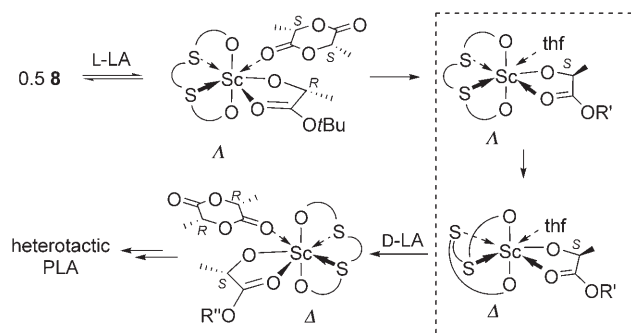
Scheme 2. Proposed mechanism for the stereocontrol in heteroselective ROP of *rac*-LA by complex **8**.

control during ROP of *rac*-LA by complex **8**. First, dimeric **8** is cleaved in the presence of excess lactide. The close contact between the "lower" *tert*-butyl and the α-methyl groups of the (*R*)-*tert*-butyl lactate in **8** blocks the coordination face below the Sc-O-C-C-O chelate ring.

A recent computational study of the β-diketiminatomagnesium initiator[10a] indicated that a stable transition state features a weak interaction between the O$_{acyl}$ atom of the approaching monomer and the coordinated C$_{carbonyl}$ atom of ring-opened LA, as well as a stronger interaction between the metal–alkoxy oxygen atom and the C$_{carbonyl}$ atom of the approaching monomer. Thus, these interactions, together with the steric repulsion between the "upper" *tert*-butyl group and the incoming lactide molecule, would favor the coordination of L-LA (*S,S* chirality, Scheme 2). After ring opening, the steric repulsion between the "upper" *tert*-butyl group and α-methyl group of the (*S*)-lactate would become pronounced. To minimize this effect, the "upper" *tert*-butyl would move away and the change in the configuration of the ligand from *Λ* to *Δ* may be triggered. The resulting species would thus favor the coordination of D-LA (*R,R* chirality), eventually resulting in heterotactic PLA. Thus, a dynamic monomer-recognition process involving interconversion of the ligand configuration from *Λ* into *Δ* would lead to high heterotactic selectivity.[15]

This assumption is further supported by the fact that the P_r value exhibited by complex **4** was much higher than that of complex **1**. From our previous study,[11a] scandium silylamido complexes with longer bridges (of three or four carbon atoms)

show high fluxionality in solution, while complexes with a C$_2$ bridge are rigid. Apparently the transformation between the *Λ* and *Δ* configurations of the ligand in complex **4**, in which there is a more flexible C$_3$ bridge, allows ready adaptation to the incoming lactide configuration (L-LA→(*S*)-lactate→*Δ* configuration→D-LA→(*R*)-lactate→*Λ* configuration).[16] This stereoregulating mechanism is somewhat different from what is commonly known as chain-end control and will be investigated in more detail in the future.

Experimental Section

Synthesis of [{(xytbmp)Sc(μ-(*R*)-(+)-OCHMeCOO*t*Bu)}$_2$] (**8**): (*R*)-(+)-*tert*-Butyl lactate (59.1 mg, 0.404 mmol) was added slowly to a solution of complex **5** (300 mg, 0.404 mmol) in toluene (15 mL) at room temperature. The colorless solution was stirred for 16 h. Then, the volatiles were evaporated under vacuum to give a white powder, which was further dried under vacuum for 2 h. The colorless solid was dissolved in pentane (30 mL) and filtered; the clear solution was then concentrated to about 10 mL at elevated temperatures. After cooling the solution to room temperature and then to −30°C, colorless crystals were formed (173 mg, 63%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ = 7.34 (d, $^4J = 2.0$ Hz, 1H, 5-H), 7.12 (d, $^4J = 2.0$ Hz, 1H, 5′-H), 6.95 (d, $^4J = 2.0$ Hz, 1H, 3-H), 6.89 (d, $^4J = 2.0$ Hz, 1H, 3′-H), 6.86 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H, Ar-H), 6.78 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H, Ar-H), 6.68 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H, Ar-H), 6.06 (d, $^3J = 7.5$ Hz, 1H, Ar-H), 5.86 (q, $^3J = 7.0$ Hz, 1H, OC*H*(CH$_3$)), 3.94 (d, $^2J = 12.5$ Hz, 1H, SCH$_2$), 3.83 (d, $^2J = 12.5$ Hz, 1H, SCH$_2$), 3.46 (d, $^2J = 13.0$ Hz, 1H, SCH$_2$), 3.34 (d, $^2J = 13.0$ Hz, 1H, SCH$_2$), 2.34 (s, 3H, 4-C*H*$_3$), 2.29 (s, 3H, 4′-CH$_3$), 1.50 (s, 9H, 6-C(CH$_3$)$_3$), 1.35 (s, 9H, 6′-C(CH$_3$)$_3$), 1.33 (d, $^3J = 7.0$ Hz, 3H, OCH(C*H*$_3$)), 0.93 ppm (s, 9H, OC(CH$_3$)$_3$); ^{13}C{^{1}H} (C$_6$D$_6$, 125 MHz): δ = 185.4 (C=O), 166.8 (C1), 160.7 (C1′), 137.9 (C6), 136.9 (C6′), 135.7 (Ar-C), 135.4 (Ar-C), 133.3 (C3), 131.0 (C3′), 128.7 (C5), 127.4 (C5′), 127.1 (Ar-C), 126.7 (Ar-C), 126.2 (Ar-C), 124.7 (Ar-C), 124.4 (C4), 124.1 (C2), 122.5 (C2′), 86.9 (O*C*(CH$_3$)$_3$), 75.1 (O*C*H(CH$_3$)), 40.9 (SCH$_2$), 39.1 (SCH$_2$), 35.3 (SCH$_2$), 34.8 (SCH$_2$), 34.4 (6-*C*(CH$_3$)$_3$) 30.5 (6-C(*C*H$_3$)$_3$), 30.3 (6′-C(CH$_3$)$_3$), 29.7 (6′-*C*(CH$_3$)$_3$) , 27.4 (OCH(*C*H$_3$)), 22.69 (OC(CH$_3$)$_3$), 21.4 (4-CH$_3$), 20.9 ppm (4′-CH$_3$). Elemental analysis calcd for C$_{74}$H$_{98}$O$_{10}$S$_4$Sc$_2$·0.66(C$_5$H$_{12}$): C 65.75, H 7.56, S 9.08; found: C 65.70, H 7.41, S 9.40.

Typical polymerization procedure: A solution of the initiator (0.5 mL, 2.9 mM) from a stock solution in THF was injected sequentially to a series of 6 mL vials loaded with *rac*-lactide (0.125 g, 0.87 mmol) and THF (0.5 mL) in a glovebox. After specified time intervals, each vial was taken out of the glovebox, aliquots were drawn and quickly quenched with *n*-pentane, with the bulk polymerization mixture quenched at the same time by adding an excess amount of *n*-pentane. All the volatiles in the aliquots were removed and the monomer conversions of the residues were determined by comparing the integrations of the methine or methyl resonances of the monomer and polymer in the ^{1}H NMR spectra (CDCl$_3$, 200 MHz). The precipitates collected from the bulk mixture were dried in air, dissolved in dichloromethane, and sequentially precipitated into methanol. The obtained polymer was further dried in a vacuum oven at 60°C for 16 h for gel-permeation chromatography (GPC) and ^{1}H,^{13}C homonuclear decoupled ^{1}H NMR analyses. In the cases where 2-propanol was used, the initiator solution in THF or toluene was treated first with a solution of 2-propanol in the same solvent for 10 min, and then injected into the solution of *rac*-lactide. Otherwise the procedures were the same.

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[13] Data for the X-ray crystal structure of **8**: $C_{74}H_{98}O_{10}S_4Sc_2$·
$3(C_6H_{14})$, $M_r = 1624.20$, $T = 110$ K, crystal size $0.6 \times 0.5 \times$
0.4 mm³, trigonal, $P3_221$ (no. 154), $a = 27.6572(11)$, $b =$
$27.6572(11)$, $c = 28.7044(16)$, $\alpha = \beta = 90°$, $\gamma = 120°$, $Z = 6$, $U =$
$19015.0(15)$ Å³, $\rho_{calcd} = 0.851$ g cm⁻¹, $\mu = 0.212$ mm⁻¹, 98698 col-
lected, 25100 unique ($R_{int} = 0.1025$), final $R_1 = 0.1005$, wR_2 [$I >$
$2\sigma(I)$] $= 0.2612$, residual electron density extremes were 1.328
and -0.653 e Å⁻³. CCDC-616875 contains the supplementary
crystallographic data for this paper. These data can be obtained
free of charge from The Cambridge Crystallographic Data
Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] a) The product from the analogous reaction of **4** and (*R*)-(+)-
tert-butyl lactate also contains a dimeric structure with both
scandium centers in a *Λ* configuration (see the Supporting
Information); b) three diastereomers, (*R,R,Λ,Λ*), (*R,R,Δ,Λ*),
and (*R,R,Δ,Δ*) are conceivable which should display distinct
resonances in the ¹H NMR spectrum as a result of the rigidity of
the structure.

[15] A similar interconversion between the *Λ* and *Δ* configurations of
the ligand in the corresponding titanium complexes has been
suggested to be responsible for the syndiotactic selectivity during
styrene polymerization; see: a) C. Capacchione, A. Proto, H.
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[16] The influence of the C_3 bridge compared with the C_2 bridge was
also observed for aluminum complexes with salen-type ligand,[3h]
where high isotactic selectivity was obtained for complexes with
a C_3 bridge.