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Polymerization of *rac*-Lactide Using Achiral Iron Complexes: A New Access to Thermally Stable Stereocomplexes

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Abstract: Enantiopure poly(lactic acid) (PLA) can form stereocomplexes when enantiomeric PLA chains are mixed in equivalent amounts. Such materials provide interesting features that might be suitable for numerous applications. Despite several advantages, the main drawback of PLA is its narrow window of processing, thus limiting its use for industrial applications. Herein, we report achiral iron complexes, that are highly active, productive and stereoselective in mild conditions for the ring-opening polymerization of lactide. The corresponding catalytic systems enable the production of stereoblock polymers with high molecular weights, allowing the formation of thermally stable and industrially relevant stereocomplexes.

Considering a decreasing feedstock and increasing economic and social pressures to reduce our dependence on petroleum, development of biocompatible and/or biodegradable polymers from renewable resources has become fertile research ground.^[1] Among the biobased polymers that have been developed during the last two decades,^[2] poly(lactic acid) (PLA) is of particular interest.^[3] This polymer, derived from 100% renewable resources, has many properties similar or superior to traditional olefin-based polymers with the added benefit of biodegradability. The availability of monomers from renewable resources has given PLA an increasing prominence in the market place. In this context, there is significant interest in methods that allow for the preparation of PLAs in a reproducible and (stereo)controlled

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fashion. It is now commonly accepted that the most efficient approach for the production of well-controlled polyesters in terms of molecular weight and microstructure is the ring-opening polymerization (ROP) of lactide (LA) with metal initiators.^[4]

Stereochemistry plays an important role in PLA, determining its physical properties and ultimately the end use of the material. Recent results indicated that the stereocontrol over polymer sequences can be an effective strategy for tuning macromolecular properties, and in particular crystallinity and biodegradability.^[5] For instance, enantiopure PLAs can form stereocomplexes when enantiomeric PLA chains are mixed in equivalent amounts.^[6] Stereocomplexation results from stereoselective interactions, mainly van der Waals forces, between two opposite stereoregular polymers which interlock to form a new material with altered physical properties as compared to the parent polymers. Stereocomplexation allows to enhance the thermal resistance, mechanical properties as well as the hydrolytic stability of PLA-based materials due to the strong interaction between L-lactic acid and D-lactic acid sequences. In particular, it has been demonstrated that enantiopure semi-crystalline homopolymers poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) form a stereocomplex melting at 230°C, which is about 50°C higher than the homochiral crystals of PLLA or PDLA.^[7] The properties and potential applications of poly(lactic acid) stereocomplexes have been extensively investigated in the last years.^[8] In particular, such materials provide interesting features that are suitable for biomedical applications (e.g., drug delivery, tissue engineering, and nanostructured surfaces).^[9] However, polymer blends of high molecular weight PLLA and PDLA are likely to form homochiral crystals of the respective polymers rather than the stereocomplex crystals.^[10] Therefore, despite the numerous advantages of PLA, one major drawback remains to be solved, namely, its narrow window of processing (i.e., the difference between its melting temperature and its degradation temperature).

Among the variety of initiators developed for the polymerization of lactide to poly(lactic acid), iron complexes are notable due to their abundance, low toxicity and biocompatibility. Inspired by the pioneering work of Hillmyer and Tolman,[11a-b] only few iron catalysts were reported for ROP of LA and most of these systems exhibit quite modest catalytic activities and productivities and proceed only at high temperatures.^[11] As a consequence, their direct use in ROP reactions is energy intensive and requires drastic conditions to drive the reaction towards high conversion and to obtain high-molecular-weight products. In this context, effective and stereoselective lactide polymerization under mild reaction conditions remains a challenge with iron complexes. As part of our ongoing effort to develop new catalysts for the ring-opening polymerization of cyclic esters,^[12,13] we report herein the synthesis and reactivity of a new class of iron complexes. Interestingly, the achiral iron

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structures, merge for the first time the three important features of high activity and high molecular weight with control of the polymer microstructure, affording the desired stereoblock PLAs. Furthermore, all three factors can be influenced by catalyst design, opening the way to a broad family of high molecular weight thermally stable PLA materials.

The monophenolate pro-ligands **1-5** described in this study were prepared in a straightforward manner, by reductive amination, following a one-pot procedure using commercially available or easily accessible starting materials (Figure 1).^[14,15] Such ligand architecture allows for steric and electronic variations on the different donor fragments (Figure 1). The new compounds **2**, **3**, **4**, and **5** were isolated with good to excellent yields. All compounds were obtained as white powders, and their identity was confirmed by NMR and high-resolution mass spectrometry or elemental analysis. All spectroscopic data of **1-5** are given in the Experimental Section.

The coordination chemistry of the ligands was studied towards an iron bisamide derivative.[16,17] Homoleptic metal precursor Fe[N(SiMe₃)₂]₂ was therefore reacted with one equiv of the neutral mono(phenol)s HL 1-5 to give the corresponding iron complexes {(L)Fe[N(SiMe₃)₂]} 6-10 in good yields (Scheme 1).^[18,19] The products were easily isolated as solids by evaporation of volatiles and washing of the residues with pentane. The compounds are air- and moisture-sensitive, readily soluble in aromatic hydrocarbons and slightly soluble in aliphatic hydrocarbons. These complexes were characterized by mass spectrometry, elemental analysis and X-ray diffraction studies for 11, which can also give the iron amido complex through a salt metathesis route. Single crystals of the new trityl-substituted complex **11** suitable for X-ray diffraction were obtained by slow evaporation of a saturated toluene solution at room temperature (Table S1). X-Ray crystallographic analysis of a single crystal of complex 11 revealed the monomeric nature of the complex in the solid state (Figure 2). Complex 11 features a five-coordinated iron centre in a distorted bipyramidal trigonal geometry. The two pyridyl groups per molecule are coordinated, together with the N and O atoms of the ligand, forming one six-membered metallacycle and two five-membered metallacycles. Therefore, the tripodal aminophenolate is actually tetradentate.



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Figure 2. Molecular structure of 11 and optimized structure of complex A. Hydrogen atoms and solvent molecule are omitted for clarity. Yellow iron, blue N, red O, green Cl.

Amido complexes 6-10 are active initiators for the controlled ROP of rac-lactide under mild conditions (Scheme 2). Representative polymerization data are summarized in Table 1. Homopolymerization of rac-lactide with the prepared metal complexes proceeds rapidly at 20°C for monomer-to-initiator ratios up to 800. Also, microstructural analysis of the different PLAs formed from rac-LA revealed that the metal complexes 6-10 exert at room temperature a significant influence on the tacticity of the polymer formed, as the microstructure is moderately to highly isotactic (up to 92% isotacticity).^[20] All values obtained from the ¹H spectra were correlated to the ones observed by ¹³C NMR (Figures S3-S10). The corresponding statistical analysis confirmed a chain-end control mechanism (Figures S3-S6, Tables S3 and S4). Thus, the stereogenic centre from the last enchained monomer unit influences the stereochemistry of monomer enchainment. This stereochemical regulation was confirmed by the observation that stereochemical errors are propagated during the polymerization process. To examine the influence of the metal centre on the microstructures of the produced PLAs, the lactide polymerization ability of complex 6 was first studied in detail. This amido complex acts as an efficient initiator for the ring-opening polymerization of

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racemic lactide under mild conditions to give isotactic PLA (Table 1, Entry 1). We assume that the environment around the iron metal centre is hindered, with all donor atoms coordinated to the metal centre.^[21] As shown in the optimized structure of complex A, the formation of five-coordinated Fe species seems to be strongly favoured. Indeed, DFT investigations showed that an isopropoxy iron complex A gives a stable five-coordinated iron species able to ring-open LA, which confirmed the geometry observed for the solid-state structure of complex 11 (Figures 2, S11 and S12).



Scheme 2. Synthesis of PLA.

With these results in hand, we were then interested in evaluating the catalytic reactivity of iron-based systems by varying different parameters (Table 1, Entries 2-5). Addition of isopropanol to the polymerization reaction resulted in better initiation efficiency and then affected the activity of the iron complexes. All the polymers produced with these in-situ generated alkoxide derivatives have narrow molecular weight distributions and number-average molecular masses (M_n) values

Table T. Polymenzation of <i>rac</i> -factore.	Table 1.	Polymerization	of rac-lactide.[a]
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close to the theoretical ones (calculated on the assumption that each isopropoxy group initiates the polymerization). These data indicate that the polymerization proceeded in a living fashion as confirmed by MALDI-TOF mass spectrometry (Figure S13). Also, changing the amido initiator by an alkoxy initiator does not affect the selectivity for isotactic PLA (Table 1, Entries 1 and 3), which is consistent with initiation of polymerization by the amido or isopropoxide group and then assistance of the ligand-metal fragment on stereocontrol.

To study the influence of the ligand substituents on the microstructures of the produced PLAs, the lactide polymerization ability of complexes 6-10 having a series of substituents was then examined. The factors investigated include steric and possible electronic effects derived from the substituents on the aromatic rings, as well as on the (potentially) pendant pyridine arm.^[12,13,22] Bulky groups were chosen as the ortho-phenolate substituent R¹ in order to favour mononuclear complex formation and increase the influence of the stereogenic centre of the last inserted monomer, which controls the stereochemistry of propagation.^[23] Complexes 7 and 8, which bears ortho-methoxy or ortho-isopropyl groups at the phenolate rings, gave relatively low selectivity for isotactic poly(lactic acid) (Table 1, Entries 5 and 6-7). This lack of tacticity is also consistent with previous observations that bulky ligands are required for stereochemical discrimination in the polymerization of rac-lactide via a chain-end control mechanism.[23]

Table 1. Po	olymerization c	of rac-lactide.[a]							
Entry	Complex	[M]/[I]/[<i>i</i> PrOH]	Time [min]	Yield ^[b] [%]	<i>M</i> n ^[c] [kDa]	PDI ^[c]	[<i>mm</i>] ^[d] [%]	$\Delta H_{m}^{[e]}$	$T_{m}^{[e]}$
1	6	200/1/0	45	83	112.5	1.32	0.84	ND	ND
2 ^[g]	6	200/1/0	90	96	73.0	1.43	0.78	ND	ND
3	6	200/1/1	20	82	24.8	1.04	0.84	29	173
4	6	800/1/1	120	65	61.5	1.08	0.83	19	162
5	7	200/1/1	1	75	16.7	1.20	0.79	ND	ND
6	8	800/1/1	1	67	51.9	1.14	0.82	21	152
7	8	800/1/1	1.5	82	79.9	1.38	0.79	14	142
8	9	400/1/1	0.5	48	29.9	1.09	0.83	27	155
9	10	200/1/1	7	93	21.3	1.14	0.68	1	136
10 ^[h]	6	100/1/1	105	84	13.5	1.16	0.91	42	193
11[]	6	100/1/1	180	43	6.7	1.16	0.92	48	195

[a] [a] All reactions performed at RT in toluene at [lactide] = 1 M. [b] As determined by the integration of 1H NMR methine resonances of lactide and PLA. [c] Mn and Mm/Mn of polymer determined by SEC-RI in THF at RT using polystyrene standards and Mn corrected by the Mark-Houwink parameter (0.58). [d] P_m is the probability of forming a new m-triad. [e] Melting temperature and enthalpy of first DSC run. Values are given in °C and J/g, respectively. [f] Not Determined. [g] Polymerization performed in THF. [h] Polymerization performed at 0 °C. [i] Polymerization performed at -10 °C

The polymerization data also indicate that, when the steric hindrance is sufficient, the ortho-substituents on the ligand do not significantly affect the ability of the initiator to control monomer enchainment; for instance, changing the ligand ortho-substituents from trityl to sec-butyl groups results in almost no change in isotacticity (Table 1, Entries 4 and 8). However, by substituting a tetradentate ligand with a tridentate ligand (complex 10, Table 1, Entry 9), we evidenced a decrease of the polymerization stereoselectivity ($P_m = 0.68$). This influence may be due to the vacant coordination site, which leads to additional monomer addition site and consequently affect the catalyst selectivity and the polymer tacticity. Finally, it appears that the temperature of the reaction can lead to a pronounced isotacticity enhancement of the resulting polymerization. Indeed, the PLAs produced by 6 at 0 °C or -10 °C is highly isotactic with Pm values of 0.91 and 0.92 respectively (Table 1, Entries 10-11).

We were then interested in studying the main thermophysical properties (glass transition temperature T_{g} , melting temperature T_{m} , melting enthalpy ΔH_{m} , crystallization temperature T_{c} , and crystallization enthalpy ΔH_c) of selected PLA samples to evaluate the influence of the polymer isotacticity. Representative values for both first and second DSC heating runs are reported in Table S5. Thermograms of the first heating runs of all samples are reported in Figure S15.

Except for the non-stereoregular PLA (Table S5, Entry 1), all samples are crystalline (Table S5, Entries 2-9), and present a single transition endotherm at high temperature (Table S6, Figure S15). Wide-angle X-ray diffraction (WAXD) analysis reveals that all polymers with $P_m \ge 0.64$ have the typical pattern of PLLA-PDLA stereocomplex crystal form, resulting from the co-crystallization of isotactic blocks of opposite configuration. The corresponding WAXD patterns are reported in Figure S17. Crystallinity, estimated by comparing the sample melting enthalpies of first DSC heating runs to melting enthalpy of crystal of infinite size (142-146 J/g),^[24] ranged from 10 to 20% for samples with P_m ranging from 0.78 to 0.84, respectively (Table S5, Entries 2-7). Although all DSC analysed samples do not crystallize from melt, samples with high isotacticity present a small exothermic peak, which is indicative of a weak crystallization phenomenon, in the second DSC heating run. The T_m values of crystalline samples of Table S5 increase linearly with the degree of isotacticity (Figure S16). A similar behaviour for PLA stereoblocks obtained from rac-LA had already been observed by Nomura (whose data are also shown in Figure S16), Du, Chen and Kol.^[25]

We also observed a correlation between the degree of stereoregularity and the glass transition temperature. Indeed, a linear relationship between T_g and P_m is apparent in Figure 4.^[26] An influence of polymer tacticity on T_g was already shown for PLAs,^[27] and T_q values ranging from 34°C and 49°C for syndiotactic^[28] and hetereotactic PLAs,^[29] respectively, were described. However, for the first time, a linear dependence between T_{q} and the degree of stereoregularity of PLAs is clearly evidenced.

As noted earlier, PLA performances in terms of durability are usually limited by thermal decomposition. However, in our case, thermal analysis revealed decomposition temperatures of up to 350°C, similar to the ones of aromatic terephthalate polyesters.[30] Degradation temperatures for all PLA samples are listed in Table S5. The significant rise in degradation temperature supports the hypothesis that the thermal stability of these isotactic PLA stereoblocks is strongly dependent on molecular weight (Figures 5 and S14). In marked contrast with what was observed for other PLA stereocomplexes, these results clearly show a strong correlation between the molecular weight and the degradation temperature and almost no correlation between the degree of stereoregularity and the degradation temperature. This dependence can be explained by an unzipping depolymerization mechanism.^[24]



Figure 5. Representative thermal degradation curves of selected samples with increasing M_n values. Selected samples are the ones from Table S5, Entry 4 $(M_n = 61 \text{ kDa}, P_m = 0.83)$, Table S5, Entry 5 $(M_n = 21 \text{ kDa}, P_m = 0.80)$, Table S5, Entry 6 (M_n = 80 kDa, P_m = 0.78), Table S5, Entry 9 (M_n = 23 kDa, P_m = 0.64).

These high molecular weight stereoblock PLAs may be useful as materials with high thermal stability for various application fields. Indeed, the main limit of industrial use of PLA



Figure 4. Plot of T_g values (from second DSC heating runs) vs. isotacticity degree for PLAs produced via ROP of rac-LA. Selected samples are the ones from Table S5. Entries 1-9.

stereocomplex crystal form is the low degradation temperature of samples obtained from equimolar mixtures of PLLA and PDLA, which, coupled with the high melting temperature of the stereocomplex crystal form, reduce the processing temperature range of this polymer. For this reason, getting highly stereoregular PLA stereoblocks having high melting and degradation temperatures represents a highly relevant industrial interest result.

We have reported a new series of iron complexes supported by readily available tripodal ligands. These iron catalysts are highly active and stereoselective in mild conditions for the ROP of lactide. The corresponding versatile systems enable the production of stereoblock polymers with high molecular weights, allowing the formation of thermally stable stereocomplexes. These results suggest a number of new avenues for industrial applications of PLA stereocomplexes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: iron • homogeneous catalysis • tacticity • polymer stereocomplex • stereoblock

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