Yttrium Phosphasalen Initiators for *rac*-Lactide Polymerization: Excellent Rates and High Iso-Selectivities

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Ⓢ *Supporting Information*

ABSTRACT: Highly active yttrium phosphasalen initiators for the stereocontrolled ring-opening polymerization of *rac*-lactide are reported. The initiators are coordinated by a new class of ancillary ligand: an iminophosphorane derivative of the popular "salen" ligand, termed "phosphasalen". Changing the phosphasalen structure enables access to high iso-selectivities (P_i = 0.84) or hetero-selectivities (P_s = 0.87). The initiators also show very high rates, excellent polymerization control, and tolerance to low loadings; furthermore, no chiral auxiliaries/ligands are needed for the stereocontrol. The combination of such high rates with high iso-selectivities is very unusual.

Polylactide (PLA) is a leading bioderived polymer sold worldwide for applications such as packaging and fiber technology, and it is an important biomedical material for wound healing, controlled release, and tissue regeneration.[1] PLA is produced from biomass and degrades to metabolites; therefore, replacing petrochemicals with PLA can reduce environmental impacts, in particular minimizing gas emissions and waste pollution.[1a] PLA is produced by ring-opening polymerization (ROP) of lactide (LA); commercially, this process is catalyzed using tin(II) octanoate. New initiators with higher activities (rates), greater degrees of polymerization control, and the ability to control the PLA stereochemistry starting from racemic LA (*rac*-LA) are much needed.[2] The stereochemistry or tacticity of PLA affects its physical and chemical properties, including its melting point, mechanical strength, degradation rate, and rheological and barrier properties.[2b] Thus, a range of polymer microstructures can be produced starting from *rac*-LA. Most initiators yield atactic or heterotactic PLA, which is useful but has undesirable thermal and mechanical properties for some applications. For example, amorphous atactic PLA has a glass transition temperature (T_g) of ~60 °C, and heterotactic PLA undergoes very slow crystallization to yield a semicrystalline polymer with a low melting temperature (T_m) of 120 °C.[2b] On the other hand, isotactic PLA is crystalline, with T_m = 170 °C for poly[(S)-LA]. Furthermore, polymerizing *rac*-LA with an iso-selective initiator can yield stereoblock/gradient PLA, a block copolymer with alternating isotactic sequences, for which T_m = 170−220 °C.[2b] This elevated T_m is due to an unusual phenomenon in which sequences/blocks of a particular enantiomer of PLA cocrystallize with the opposite enantiomer, giving rise to a double-helical stereocomplex microstructure with

improved properties.[3] Despite many reports of new initiators, there remain only a few able to produce isotactic PLA from *rac*-LA.[2] Among the iso-selective initiators reported previously, the majority of studies focused on Al−salen complexes and their derivatives.[4] Since the first reports, much attention has focused on Al[5] and other group 13 initiators.[6] Although their optimized iso-selectivities (P_i) exceed 0.9, these initiators are all marred by low rates of polymerization (typically taking days to reach completion), the need for high initiator loadings (typically ~1 mol %) and a narrow range of operating conditions (temperatures >70 °C in toluene solution). Examples of iso-selective initiators using elements other than those in group 13 remain extremely rare.[7] One very interesting example is the homochiral yttrium phosphine oxide alkoxide complex reported by Arnold and co-workers, for which P_i = 0.81 at 288 K.[8]

We are interested in iminophosphorane (N=P) ligands as alternatives to conventional imine-based ligand systems.[9] Concurrently, we have observed that yttrium- and lanthanide-based LA polymerization initiators show significantly higher rates with electron-donating ligands.[10] Conventionally, increased activity has been expected upon substitution of Lewis acidic initiators with electron-withdrawing functionalities.[2] To investigate further the electronic influence of the ancillary ligand, we targeted iminophosphorane analogues of the ubiquitous salen ligands. We have named these new ligands "phosphasalens". Earlier this year, we reported the first examples of yttrium phosphasalen alkoxide complexes, which proved to be effective LA polymerization initiators.[11] Herein we report the new phosphasalen initiators **1−3** (Figure 1), which operate with very high rates and can exert high degrees of stereocontrol.

The proligands L^1 and L^2 were synthesized according to modifications of published procedures [see Schemes S1 and S2 in the Supporting Information (SI)].[11] Initiators **1−3** were prepared by addition of stoichiometric amounts of KN(SiMe$_3$)$_2$ to slurries of the corresponding proligands in tetrahydrofuran (THF). This gave colorless suspensions after 4 h. The reactions were monitored using ^{31}P{^{1}H} NMR spectroscopy, which showed significant shifts in the singlet signals from 41.8 to 24.2 ppm for L^1 and 40.1 to 20.3 ppm for L^2 (R^2 = OMe). This indicated the clean formation of the anionic potassium salts. Addition of [YCl$_3$(THF)$_{3.5}$] gave products that showed just one singlet in the ^{31}P{^{1}H} NMR spectra at 35.0 and 31.5 ppm,
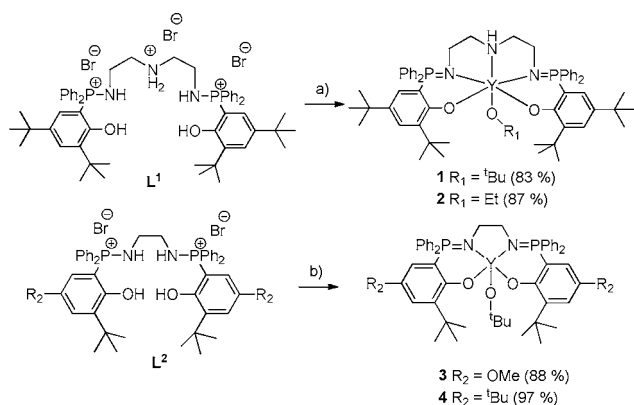
Figure 1. Syntheses and structures of initiators **1−4**. Conditions: (a) (i) 5 equiv of $KN(SiMe_3)_2$, THF, 4 h, 298 K; (ii) $[YCl_3(THF)_{3.5}]$, THF, 4 h, 298 K; (iii) KOR_1, THF, 7 h, 298 K. (b) (i) 4 equiv of $KN(SiMe_3)_2$, THF, 4 h, 298 K; (ii) $[YCl_3(THF)_{3.5}]$, THF, 4 h, 298 K; (iii) KO^tBu, THF, 4 h, 298 K.

Table 1. Polymerization Data for Initiators 1−4

	T (K)	t (min)	conv. (%)[f]	M_n (kg/mol)[g]	M_n^{calc} (kg/mol)	PDI	P_i^h
1[a]	298	30	87	210	62.6	1.09	0.76
1[b]	298	56	92	41.0	66.2	1.05	0.74
1[c]	298	17	92	12.8	13.2	1.03	0.77
1[c]	258	180	77	16.0	11.1	1.01	0.84
2[a]	298	48	85	61.7	61.2	1.04	0.72
2[d]	273	60	71	15.5	10.2	1.01	0.73
2[d]	258	180	73	13.5	10.5	1.01	0.81
3[e]	298	0.33	88	165	126.7	1.50	0.13
4[e]	298	0.75	97	223	140	1.34	0.14
4[e]	298	1.1	80	115	105	1.08	0.10

[a]THF, [**I**]:[LA] = 1:500, [LA] = 1 M. [b]Same as a except that 1 equiv (vs **1**) of ^iPrOH was added. [c]THF, [**I**]:[^iPrOH]:[LA] = 1:1:100, [LA] = 0.5 M. [d]THF, [**I**]:[LA] = 1:100, [LA] = 0.5 M. [e]THF, [**I**]:[LA] = 1:1000, [LA] = 1 M. [f]Determined by integration of the methyne region of the ^1H NMR spectrum (LA, 4.98−5.04 ppm; PLA, 5.08−5.22 ppm). [g]Determined by SEC-MALLS in THF. [h]Determined by analysis of all of the tetrad signals in the methyne region of the homonuclear-decoupled ^1H NMR spectrum.

respectively, indicating quantitative conversion to the yttrium halide complexes. Salt metatheses using KOEt or KO^tBu yielded **1−3**, which also showed singlets in the $^{31}P\{^1H\}$ NMR spectra at 33.4 (**1**), 34.2 (**2**), and 31.6 (**3**) ppm. The new initiators were also fully characterized using ^1H and $^{13}C\{^1H\}$ NMR spectroscopies and elemental analyses.

Crystals of compound **1** suitable for X-ray crystallography were obtained by evaporation from pentane (Figure 2). **1** is
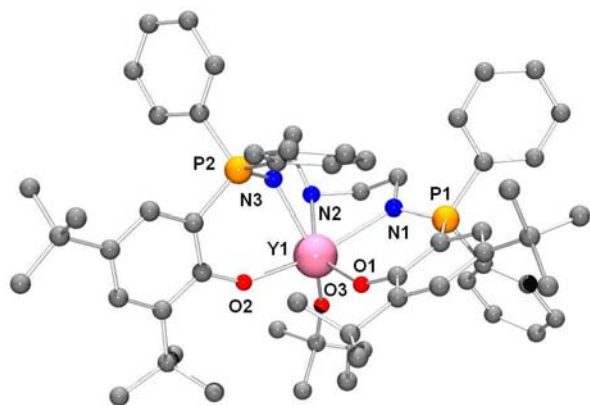

Figure 2. Molecular structure of **1**.

monomeric in the solid state, with coordination of the additional NH donor to give a hexacoordinate Y center. The *tert*-butoxide and one of the phenoxide O atoms occupy the axial positions; the phosphasalen adopts a β-cis configuration. Selected bond lengths and angles are given in Table S2 in the SI.

Compounds **1−3** were all highly active and controlled initiators for ROP of *rac*-LA, and the ligands' structures influenced the reactivity (Table 1). The polymerizations were all conducted in THF at $T \leq 298$ K. The choice of solvent was important, as the initiators were not tolerant of CH_2Cl_2 and a homogeneous solution did not form in toluene at 298 K. Aliquots were regularly removed and analyzed using ^1H NMR spectroscopy for % conversion and size-exclusion chromatography with multiangle laser light scattering (SEC-MALLS) for number-average molecular weight (M_n) and polydispersity index (PDI). The PLA stereochemistry was assessed by comparison of the tetrad resonances observed in the homonuclear-decoupled ^1H

NMR spectra with the values predicted by Bernoullian statistics (Figure 3 and Figure S4 in the SI).[12] The resolution of the
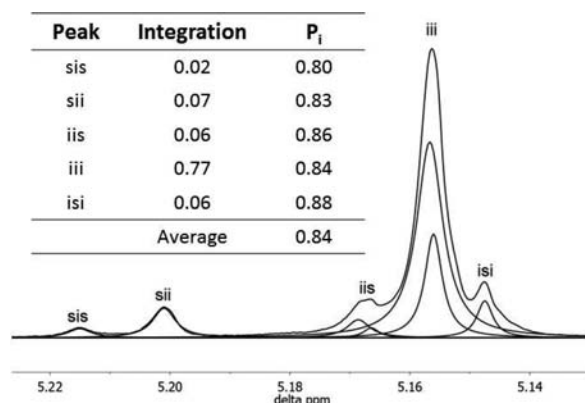

Peak	Integration	P_i
sis	0.02	0.80
sii	0.07	0.83
iis	0.06	0.86
iii	0.77	0.84
isi	0.06	0.88
Average		0.84

Figure 3. Methyne region of the homonuclear-decoupled ^1H NMR spectrum of isotactic PLA produced using initiator **1** ([**1**]:[iPrOH]: [LA] = 1:1:100, [LA] = 0.5 M, THF, 258 K).

integrals for the peaks corresponding to the *iis*, *iii*, and *isi* tetrads was improved using peak deconvolution methods. The P_i values were determined for all five tetrads, and their average was used as the P_i for the initiator (Table 1). We were very interested to observe high stereoselectivities with all of the initiators and, in particular, the high iso-selectivities of **1** and **2**.

The initiator activities were very high. In fact, the initiators were so effective that low loadings and high dilutions were needed in order to monitor the polymerizations effectively. Initiators **1** and **2** showed nearly complete conversion of 500 equiv of LA in ~1 h. It is interesting to note the compounds' high activity in comparison with other reported yttrium complexes featuring salens or closely related derivatives as ligands (Figure 4), all of which tend to be quite active polymerization initiators.[2]

The Y−salen initiator **5** required 14 h to reach complete conversion at a higher initiator loading (1 mol %).[4a] Y−half-salen complex **6** (1 mol %) required 3 days to reach complete conversion.[5d] Qualitatively, initiators **1** and **2** have the same activity as the recently reported Y−salen initiator **7**,[13] which was notable for its high rates. It is important to note, however, that **7**

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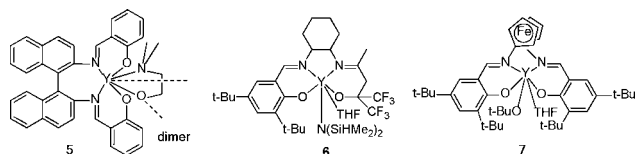dx.doi.org/10.1021/ja310003v | *J. Am. Chem. Soc.* 2012, 134, 20577−20580

Figure 4. Structures of other high-activity yttrium initiators.

lacks any tacticity control in *rac*-LA ROP. Analysis of the conversion versus time data for **1** and **2** indicated a first-order dependence of the polymerization rate on the LA concentration, and pseudo-first-order rate constants $k_{obs} = 6.9 \times 10^{-4}$ and $7.9 \times 10^{-4}\ s^{-1}$ (0.2 mol %, [LA] = 1 M, THF) were obtained (Figure S2). Initiators **3** and **4**, on the other hand, exhibited even greater activity; it took just seconds to reach complete conversion even at 0.1 mol % loading. Thus, these phosphasalen initiators show some exceptionally high activities and significantly higher rates than analogous Y−salen initiators. As iminophosphoranes are strong σ and π donors, phosphasalen ligands are expected to be more electron-donating than their salen counterparts.[10b,d,11] It is interesting that the more electron-donating ligands accelerate the polymerization rate. This can be rationalized by considering that reducing the Lewis acidity of the Y center may labilize the Y−alkoxide bond. It is this latter bond that is central to efficient polymerization, as it is the propagating species in the coordination−insertion mechanism. Thus, electron-donating ligands may accelerate the reaction by increasing the rate of LA insertion. A related mechanistic hypothesis was elegantly investigated by Tolman and Hillmyer very recently.[14] They used it to rationalize the activity of a series of phenolate aluminum initiators of ε-caprolactone polymerization. Our findings illustrate the potential for other new ligands and metal centers substituted with electron-donating substituents to accelerate polymerization rates.

Initiator **1**, which has a *tert*-butoxide coligand, showed very high rates but rather less impressive polymerization control. The experimentally observed M_n (200 kg/mol) far exceeded that predicted on the basis of the reaction stoichiometry (63 kg/mol), likely because of relatively slower initiation (vs propagation) using the sterically hindered *tert*-butoxide coligand. To overcome this, we added 1 equiv of ^{i}PrOH, which would be expected to undergo rapid and reversible alcoholysis reactions, thereby enabling efficient initiation and controlled polymerization. Indeed, the addition of ^{i}PrOH greatly improved the polymerization control, giving M_n values (41.0 and 12.8 kg/mol) close to those predicted on the basis of the initiator loading (66.2 and 13.2 kg/mol, respectively). In every case, the PDI was narrow (<1.10), also indicative of good control. Initiator **2**, which has an ethoxide coligand, showed excellent polymerization control without the need for any exogeneous alcohol, again supporting the notion that less sterically hindered alkoxide coligands enable more rapid initiation. Thus, 500 equiv of LA was polymerized using **2** to yield PLA with $M_n = 61.7$ kg/mol ($M_{n\ calc} = 61.2$ kg/mol) and PDI = 1.04. When the reaction temperature was lowered, the polymerizations remained very well controlled, yielding PLA with $M_n = 15$ kg/mol and PDI = 1.01 even at 258 K. Figure S3 illustrates the linear evolution of M_n versus conversion for both initiators **1** (with 1 equiv of ^{i}PrOH) and **2**, providing further evidence of their good polymerization control. Initiators **3** and **4** showed slightly broader PDI values, in line with the exceptionally high rates and the *tert*-butoxide initiating group. The polymerization control could again be improved by addition of 1 equiv of ^{i}PrOH.

All three initiators showed high degrees of stereocontrol, and unexpectedly, they also showed a distinct difference in PLA tacticity. Initiators **1** and **2** yielded highly isotactic PLA (P_i = 0.84 for **1** at 258 K; Figure 3), while initiators **3** and **4** yielded highly heterotactic PLA ($P_s > 0.87$). At 298 K, **1** and **2** showed P_i values of 0.74 and 0.72, respectively. It should be noted that initiators capable of yielding such P_i values under ambient conditions remain rare.[6a,8b,15] To exploit their promising properties, the polymerizations were conducted at a lower temperature (258 K), and even higher P_i values (0.84 and 0.81, respectively) were observed. Furthermore, the polymerization rates remained high, and the polymerization control was excellent. In the case of **1**, the addition of ^{i}PrOH that was necessary to improve the polymerization control had a negligible influence on P_i; this is interesting, as it shows that high degrees of stereocontrol are also possible in the presence of a chain-transfer agent. Polymerizations using **3** resulted in highly heterotactic PLA ($P_s = 0.87$), similar to the value observed previously for **4** ($P_s = 0.9$).[11] Thus, it is clear that modification of the electronic properties of **3** relative to **4** did not diminish the high tacticity control. The mechanism for heteroselectivity involves chain-end control (CEC), where the stereochemistry of the last inserted LA enantiomer dictates the coordination/insertion of the subsequent enantiomer.

To understand the unusual iso-selectivity exhibited by **1** and **2**, we analyzed the relative intensities of the stereoerror tetrad signals in the PLA produced by them (Figure 3). The *sii:iis:isi* signal intensity ratio was 1:1:1, in line with a CEC mechanism and synthesis of stereoblock PLA. Analysis of the polymer by differential scanning calorimetry showed a T_m value of 178 °C, further confirming the formation of a stereoblock polymer.[16] Most iso-selective initiators operate by a site-control mechanism, wherein chiral (or racemic) initiators select for particular enantiomers of LA. There are a few examples of Al initiators that are iso-selective as a result of a CEC mechanism, most notably the Al−salen systems reported by Nomura[5h,n] and others[5b,f,17] and the Al−salan complexes reported by Gibson.[5i,k]

In an attempt to understand the contrasting tacticity control of initiators **1** and **2** versus **3** and **4**, the initiator structures were investigated. The solid-state structure of **4** was reported previously; it crystallizes as a mononuclear complex in which the Y center exhibits a square-pyramidal geometry with the phosphasalen ligand occupying the basal plane and the alkoxide the apical position.[11] All of the NMR spectra of **3** and **4** are closely related, and several signals are indicative of a mononuclear solution structure, most notably the observation of just one singlet signal in the $^{31}P\{^1H\}$ NMR spectrum and the equivalence of the quaternary phenolate carbon signals in the $^{13}C\{^1H\}$ NMR spectrum. Variable-temperature (VT) ^1H NMR measurements on solutions of **3** indicated significant fluxionality on the NMR time scale that could not be sufficiently resolved even at 188 K. The rotational Overhauser effect spectroscopy (ROESY) NMR spectrum showed exchange between the phenyl substituents on the iminophosphorane functionalities, also indicative of solution fluxionality.

In contrast, in the solid-state structure of **1**, Y has a distorted octahedral geometry and is coordinated by the additional NH substituent. The N1−O1−N2−O2 dihedral angle is 166.38°, indicating a significant deviation from planarity compared with the pentacoordinated complex **3**. Diffusion-ordered spectroscopy (DOSY) NMR experiments using **1** in THF solution provided an estimated hydrodynamic radius (R_h) of 4.5 Å, in reasonable agreement with the value estimated from the X-ray crystal structure of **1** (6.0 Å) (Figure 2). Crystals of **2** could not be

isolated, but an X-ray diffraction experiment on a degradation product of **2** was successful (Figure S1). This partially hydrolyzed species is a dimer wherein the two Y cores are bridged by both an alkoxide and a hydroxyl coligand, the latter presumably arising from exposure to adventitious water. Also, the additional NH donor in the ligand backbone is coordinated to each Y center. The coordination geometry at each Y center is monocapped trigonal-prismatic. From the X-ray structure of the partially hydrolysed dimer of **2**, an R_h of 8.9 Å was obtained (see the SI). These findings indicate that **1** and **2** are likely to adopt mononuclear structures in THF solution. VT ^{1}H NMR studies using **1** also indicated some degree of fluxionality, but the ROESY spectrum showed no exchange between the iminophosphorane substituents, consistent with a more constrained structure.

In any case, the coordination geometries of **1** and **2** are quite different from those of **3** and **4**, with the former containing a hexacoordinate Y and the latter a pentacoordinate Y. Thus, we tentatively attribute the iso-selectivity observed with **1** and **2** to their more sterically congested and constrained active sites compared with **3** and **4**. Such a finding is in line with Nomura's hypothesis regarding CEC observed with Al−salen complexes.[5h] Further studies aimed at understanding the detailed mechanisms of iso-selectivity are underway.

In conclusion, we have reported the first example of a highly iso-selective and highly active yttrium phosphasalen initiator. These initiators show very high rates, excellent polymerization control, tolerance to low loadings, and high iso-selectivities. When the phosphasalen ancillary ligand was changed, the high rates were maintained, but the stereocontrol changed to highly heterotactic. The new initiators do not require any chiral ancillary ligands or complexes and operate by CEC mechanisms.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Detailed experimental protocols, X-ray data (CIF), polymerization data and figures, and DOSY calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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20580

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