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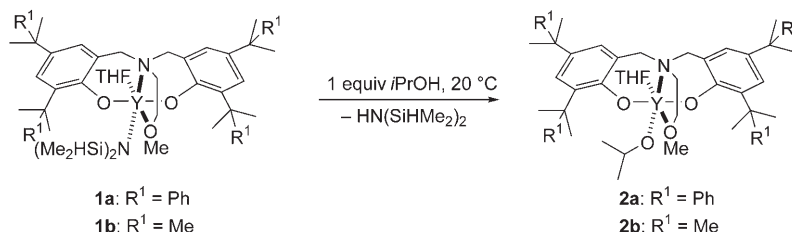
Highly Active, Productive, and Syndiospecific Yttrium Initiators for the Polymerization of Racemic β -Butyrolactone**

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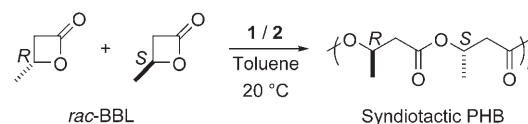
Biodegradable polymers have recently gained great attention as a replacement for conventional synthetic materials.^[1] Among the new biodegradable polymers that have been developed during the last decade,^[2] polyhydroxyalkanoates (PHAs) are of particular interest.^[3] These materials combine the film-barrier properties of polyesters with the mechanical performance properties of petroleum-based polyethylene and polypropylene. The most common PHA is poly(3-hydroxybutyrate) (PHB), which is an isotactic, highly crystalline thermoplastic polyester produced by various bacteria and algae. One of the most convenient and promising synthetic routes to PHAs uses metal initiators to effect the ring-opening polymerization (ROP) of β -butyrolactone (BBL), where the relief of ring strain is the driving force for polymerization.^[2a] Highly isotactic (*R*)- or (*S*)-PHB can be obtained when optically pure (*R*)- or (*S*)-BBL is involved,^[4] while use of a racemic (*rac*) mixture of BBL gives rise to atactic PHB^[5] and PHB enriched in isotactic^[6] or syndiotactic^[7] diads. However, most initiators are extremely slow and produce low-molecular-weight PHB. Although some initiators polymerize BBL with excellent rates,^[8] stereospecific polymerization of *rac*-BBL remains a challenge. Recently, we reported that well-defined single-site bis(phenolate) complexes of Group 3 metals are highly active initiators in the synthesis of heterotactic and syndiotactic poly(lactic acid) from *rac*-lactide and *meso*-lactide, respectively.^[9] Herein, we

report a highly active and stereoselective initiator for the polymerization of *rac*-BBL, generating highly syndiotactic PHB.

The high lactide polymerization activities observed with the yttrium initiators **1a,b** and **2a,b** led us to investigate these complexes for the ROP of *rac*-BBL (Scheme 1 and Scheme 2).^[9b] The solution-state structures of **1a** and **2a** were recently reported,^[9b] and these structures are now supported by the X-ray crystal structure of **1a** (Figure 1).^[10] Complex **1a**



Scheme 1. Synthesis of complexes **1** and **2**.



Scheme 2. Synthesis of syndiotactic PHB.

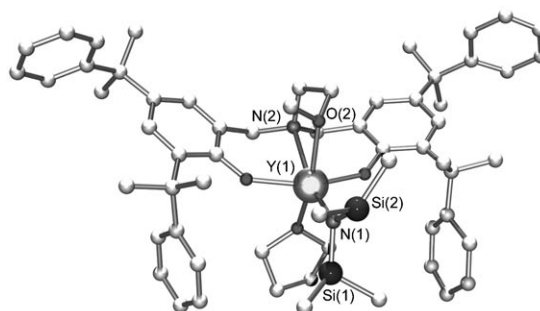


Figure 1. Crystal structure of complex **1a**; all hydrogen atoms and solvent molecules are omitted for clarity.

adopts a distorted octahedral coordination geometry about the yttrium atom with all four donors of the bis(phenolate) ligand bound to the metal center. One THF ligand and one bis(dimethylsilyl)amido group occupy the remaining *cis* positions.

Initial polymerizations were performed using 0.5 mol % of **1a,b** or in situ generated **2a,b** with commercially available *rac*-BBL. Complexes **1a,b** and **2a,b** are active initiators for the controlled ROP of *rac*-BBL under mild conditions. However, as polymerizations of *rac*-BBL with **2a,b** proceed more rapidly than with **1a,b**, we decided to explore this reaction by using the former complexes (Table 1).^[11] We observed a strong influence of the solvent. For [BBL]/[**2a**] = 200, polymerization in toluene and chlorobenzene reached 97% conversion in less than 1 minute (Table 1, entries 1, 2),

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Table 1: Syndiospecific polymerization of *rac*-butyrolactone.^[a]

Entry	Complex	[BBL]/[Y]	[BBL] [M]	Solvent	t [min]	Yield [%] ^[b]	<i>M</i> _n [g mol ^{−1}] ^[c]	PDI ^[c]	<i>P</i> _r ^[d]	<i>T</i> _m [°C] ^[e]
1	2a	200	2.44	Toluene	1	98	22 600	1.15	0.88	154
2	2a	200	2.44	C ₆ H ₅ Cl	1	95	24 600	1.15	0.84	158
3	2a	200	2.44	THF	120	98	27 400	1.03	0.83	133
4	2a	400	2.44	Toluene	1	98	26 100	1.06	0.89	157
5	2a	400	1.00	Toluene	10	98	37 400	1.14	0.90	167
6	2a	400	4.80	Toluene	4	95	36 100	1.08	0.87	150
7 ^[f]	2a	400	1.00	Toluene	720	98	37 100	1.10	0.94	178
8	2a	600	2.44	Toluene	5	98	47 200	1.10	0.88	155
9	2a	1000	neat	–	5	95	48 600	1.16	0.81	142
10	2a	2000	8.80	Toluene	18	87	39 900	1.18	0.87	156
11	Y[N(SiHMe ₂) ₂] ₃ (THF) ₂	400	2.44	Toluene	4320	94	27 700	1.22	0.55	95
12	“Y(OiPr) ₃ ”	400	2.44	Toluene	120	95	26 400	1.27	0.51	91
13	2b	400	2.44	Toluene	2	95	33 900	1.10	0.81	138

[a] All reactions were performed at 20 °C (except for Entry 7). [b] As determined by the integration of methine ¹H NMR resonances of *rac*-BBL and PHB. [c] *M*_n and *M*_w/*M*_n of polymer determined by size-exclusion chromatography in CHCl₃ at room temperature using polystyrene standards. PDI = polydispersity index. [d] *P*_r is the probability of racemic linkages between monomer units and is determined from the carbonyl region of the ¹³C{¹H} NMR spectrum. [e] Determined by differential scanning calorimetry (DSC; second scan). [f] Reaction run at −20 °C.

while polymerization in THF led to 98 % conversion within 2 h (Table 1, entry 3). Decreasing the concentration of monomer resulted in a substantial decrease in the rate of polymerization (Table 1, entries 4, 5). All other polymerization reactions were therefore preferably conducted in toluene at a concentration of *rac*-BBL of 2.44 M. Several reactions were also performed by changing the monomer-to-metal ratio. For instance, complete conversion of 400 equivalents of *rac*-BBL was achieved within 1 minute at room temperature (turnover frequency, TOF = 24 000 h^{−1}; Table 1, entry 4). The activity of this system is thus more than one order of magnitude higher than that of yttrium 2-methoxyethoxide as previously reported by Spassky and co-workers under similar conditions.^[12] To confirm the influence of the bis(phenolate) ligand on the activity, control experiments were carried out with Y[N(SiHMe₂)₂]₃(THF)₂ and “Y-(OiPr)₃” (generated in situ) as initiators (Table 1, entries 11, 12). The results show that **2a** indeed displays a significantly higher activity than the two reference systems when polymerizations are carried out in toluene. The yttrium alkoxide **2a** can polymerize 1000 equivalents of monomer within 5 minutes at 20 °C in neat BBL resulting in TOF = 12 000 h^{−1} (Table 1, entry 9), and 2000 equivalents at high concentrations of monomer in less than 20 minutes (TOF = 6000 h^{−1}; Table 1, entry 10).

For [BBL]/[**2a**] < 1000, the resultant polymers reveal narrow molecular-weight distributions and experimental number-average molecular masses (*M*_n) close to the theoretical ones. However, for higher ratios, experimental *M*_n values do not correspond well with calculated *M*_n values. This mismatch possibly arises from chain-transfer processes or poor correlation between the polystyrene calibration of the gel permeation chromatograph and the actual molecular weights of the PHB chains, as already reported by Coates and co-workers.^[8]

Microstructural analysis by ¹³C NMR spectroscopy of the different PHBs formed from *rac*-BBL revealed that complexes **2** exert a significant influence at room temperature on the tacticity of the polymer formed (Scheme 2). On the basis

of prior ¹³C NMR assignments of the carbonyl region of PHB, the upfield and downfield signals in the carbonyl region correspond to the *meso* (*m*) diad sequences, *R*–*R* and *S*–*S*, and the racemic (*r*) diad sequences, *R*–*S* and *S*–*R*, respectively.^[13] Our PHBs feature a strong contribution correlating to *r*-centered diads (δ = 169.16 ppm), indicative of syndiotactic PHB (Figure 2). Expansion of the methylene region shows

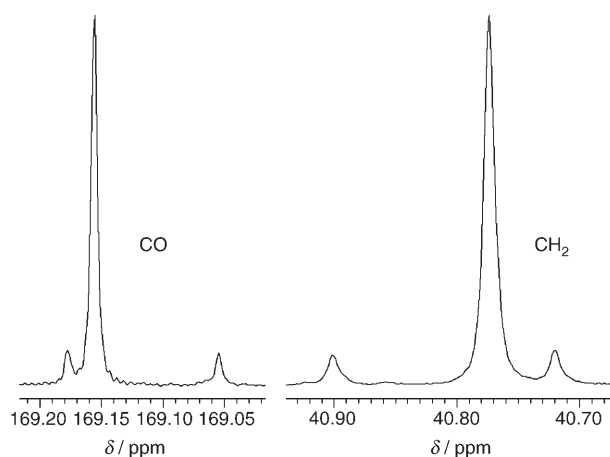


Figure 2. Carbonyl and methylene regions of the ¹³C NMR spectrum (125 MHz, CDCl₃, 40 °C) of PHB prepared by polymerization of *rac*-BBL using complex **2a** (see Table 1, entry 7).

four peaks that correspond to triad sensitivity (Figure 2). We correlated the most intense resonance at δ = 40.77 ppm to the *rr* triad, and we attributed the resonances at δ = 40.72 and 40.90 ppm to the *mr* and the *rm* triads, respectively. The remaining *mm* triad at δ = 40.85 ppm is almost negligible.^[14] Statistical analysis confirms a chain-end control mechanism (See Supporting Information). We observed differences in the microstructure of the PHBs depending on the nature of the solvent. While polymerization of *rac*-BBL in toluene gave PHB with nearly 90 % of syndiotactic enchainment (Table 1, entry 1), polymerizations in THF and chlorobenzene gave

83% and 84%, respectively, of syndiotacticity (Table 1, entries 2 and 3). At -20°C , polymerization proceeded slowly but the resulting PHB revealed a higher degree of syndiotacticity ($P_r=0.94$; Table 1, entry 7). As already observed for the polymerization of *rac*-lactide,^[9b] complex **2b**, which bears *tert*-butyl groups at the phenolate rings, reveals a lower selectivity for syndiotactic PHB ($P_r=0.81$; Table 1, entry 13). This decrease in tacticity is consistent with previous observations that ligand substituents are primordial for stereochemical control through a chain-end control mechanism.^[15]

DSC measurements of selected PHB samples showed the strong influence of the stereochemistry on the melting temperature (T_m), which increases with the degree of syndiotacticity (Table 1, entries 2, 7, 9, 10). For the most syndiotactic polymer, T_m is around 178°C , that is, the highest melting temperature reported so far for syndiotactic PHB.^[13,16] The DSC traces display a single, sharp transition endotherm at high temperature, demonstrating the formation of a uniform crystalline ordering in the solid state, which may indicate a narrower dispersion of stereochemical chain sequences.

It is well established that the ring opening of BBL by metal alkoxides can proceed by a coordination–insertion mechanism or an anionic mechanism.^[8] To determine the route involved in the ROP of BBL with **2a**, reactions were conducted with [BBL]/[Y] ratios of less than 10. The unambiguous identification by ^1H NMR spectroscopy of the $-\text{OCH}(\text{CH}_3)_2$ end group at $\delta=5.00$ ppm confirmed that the BBL ring is cleaved at the acyl–oxygen bond and inserted into the metal–isopropoxide bond. Furthermore, *trans*-crotonate (and carboxy) groups were not observed in the ^1H NMR spectrum, confirming the coordination–insertion mechanism. Indeed an anionic mechanism leads generally to a high concentration of crotonate.^[8]

In conclusion, the yttrium alkoxide complex **2a** exhibits the highest activity and greatest stereoselectivity for syndio-specific polymerization of *rac*-BBL to date. These results suggest a number of new avenues for biodegradable polymers.

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