Syndiotactic-Enriched Poly(3-hydroxybutyrate)s via Stereoselective Ring-Opening Polymerization of Racemic β-Butyrolactone with Discrete Yttrium Catalysts

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ABSTRACT: The mechanism of the ring-opening polymerization of *rac*-β-butyrolactone using yttrium complexes supported by dianionic aminoalkoxybis(phenolate) ligands as initiators has been investigated by NMR and shown to occur via a coordination-insertion pathway. The microstructure of the resulting syndiotactic-enriched poly(3-hydroxybutyrate)s (PHBs, P_r up to 0.94) has been studied by ^{13}C NMR spectroscopy, enabling a detailed assignment of resonances at the diad and triad levels. On this basis, a statistical Bernoullian analysis has been performed which evidenced that syndioselectivity originates from a chain-end control. Some thermal properties of these PHBs have been studied by WAXD and thermoanalytical techniques and shown to be markedly affected by the syndiotacticity degree. This is especially the case for the melting temperature which raises up to 183 °C for $P_r = 0.94$, a temperature higher than that of pure isotactic PHB (ca. 180 °C).

Introduction

Biodegradable polymers have recently gained much interest as a replacement for conventional oil-based materials.[1] Among the most promising candidates in this class of materials are aliphatic polyesters, and in particular, poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and poly(hydroxyalkanoate)s (PHAs). These polymers have been shown to be nontoxic and biocompatible both as polymers and as their degradation products, for which degradation, in most cases, occurs naturally in the body.[2] They have a range of pharmaceutical and biomedical uses based on these characteristics and their physicochemical properties.[3] PLA and PGA, which are used as absorbable suture material, are hydrolyzed in vitro and in vivo within days, while PHAs are broken down much more slowly. However, although their rate of abiotic hydrolysis is relatively slow, PHAs have the most potential, because their microbial hydrolysis is more rapid and can be manipulated by variations in processing techniques, molecular weight of the polymer, copolymer composition and blending.[4]

The most common PHA is natural poly(3-hydroxybutyrate) (PHB), which is an isotactic, highly crystalline thermoplastic polyester produced by various bacteria and algae. Another efficient synthetic route 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. Although most initiating systems produce low molecular weight PHB and are extremely slow, Coates and coworkers described that discrete β-diiminate zinc alkoxide complexes are able to polymerize racemic BBL with good rates under mild conditions to make PHBs in a controlled manner.[5] High molecular weights are obtained at room temperature with a fairly good polydispersity, though the PHBs produced are all atactic. In fact, examples of stereospecific ROP of BBL remain rare. Highly isotactic (*R* or *S*) PHB can be obtained when optically pure (*R*)- or (*S*)-BBL is involved,[6] while using *rac*-BBL, atactic PHB[7] and PHB enriched in isotactic[8] or syndiotactic[9] diads can be formed. In 1989, Spassky et al. reported the isospecific ROP of *rac*-BBL using a Et_2Zn/(*R*)-3,3-dimethylbutane-1,2-diol catalyst to give optically active PHB.[10] The 46% ee of the unreacted enantiomer revealed that the catalyst preferentially polymerizes (*R*)-BBL at low conversion. The first demonstration of syndiospecific ROP of *rac*-BBL with tin initiators was reported by Gross et al. in 1993.[11] The polymerization was carried out with Bu_3SnOMe to give low molecular weight PHB enriched in syndiotactic dyads ($P_r = 0.70$). More recently, Hori[9a] and Giani-Beaune[12] reported a distannoxane catalyst that affords a predominantly syndiotactic PHB ($P_r = 0.67$) by a chain-end control mechanism. A better control of the polymerization allowed achieving higher molecular weight PHB at 40 °C within 95 h.

We have recently investigated the synthesis and characterization of well-defined achiral group 3 metal complexes supported by aminoalkoxybis(phenolate) ligands.[13] Some of these complexes, i.e., yttrium amido and alkoxide derivatives, have shown quite interesting performance for the heterotactic living polymerization of *racemic* lactide (*rac*-LA).[14] With these systems, narrow molecular weight distributions and number-average molecular weights (M_n) dictated by monomer-to-initiator ratios were observed, indicative of living polymerizations. More, minor changes in the ligand architecture resulted in dramatic enhancements in polymerization rates and selectivities. The latter stereoselectivities in favor of heterotactic PLA were demonstrated to arise from a chain-end control mechanism[14b,c]

On the basis of this success for lactide polymerization, we envisioned the use of these group 3 aminoalkoxybis(phenolate) systems to prepare PHBs and reported the first highly syndio-

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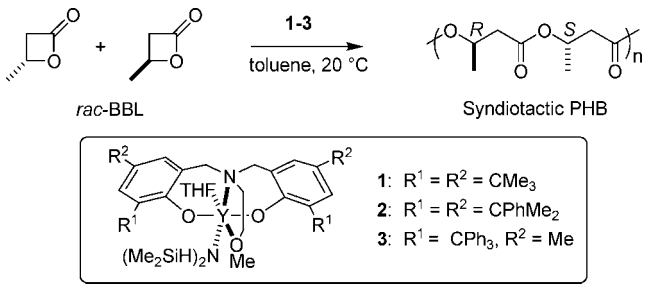
Scheme 1. Synthesis of Syndiotactic-Enriched PHB by ROP of *rac*-BBL with Aminoalkoxybis(phenolate) Yttrium Alkoxide Initiators 1−3



tactic living polymerization of *rac*-BBL.[15,16] As an extension of our interest in this field, we have studied the controlled ROP of *rac*-BBL by using different highly active and stereoselective yttrium derivatives as initiators. We report in this paper the mechanism involved during the polymerization reaction and the microstructure of the polymeric chains, which have been established on the basis of detailed NMR analyses. We describe also some thermal properties of the corresponding PHBs as a function of the degree of syndiotacticity.

Results and Discussion

Ring-Opening Polymerization of *rac*-β-Butyrolactone with Aminoalkoxybis(phenolate) Yttrium Amido Initiators. The ROP of *rac*-BBL was investigated with aminoalkoxybis(phenolate) yttrium amido complexes [(L)M(N(SiHMe$_2$)$_2$)(THF)] **1**−**3** (Scheme 1), which differ in the nature of substituent at the *ortho*-phenolate positions. These complexes were prepared in a straightforward manner in good yields by reaction of Y[N(SiHMe$_2$)$_2$]$_3$ with 1 equiv of the corresponding bis(phenol) pro-ligands H_2L.[13,17] The polymerization of *rac*-BBL with these yttrium complexes proceeds rapidly under mild conditions. As summarized in Table 1 with representative examples, all complexes proved to be active, allowing full conversion of 200−600 equiv of *rac*-BBL in 1−60 min at 20 °C in toluene solutions at [*rac*-BBL] = 1.0−4.8 mol·L^{-1}, eventually offering high molecular weight PHBs. Reactions proceeded in a living fashion, as evidenced by the narrow polydispersities and the good match between experimental and calculated M_n values, calculated on the assumption that a single PHB chain is produced per metal center via initiation of the polymerization by the aminoalkoxybis(phenolate) yttrium amido complexes.[18] The ROP of *rac*-BBL promoted by complexes **1**−**3** allowed the formation of highly syndiotactic-enriched PHBs, with a probability of *racemic* linkages between monomer units (P_r) in the range 0.80−0.94 (Table 1, entries 1−8) (*vide infra*). We observed significant differences in the PHB microstructures depending on the nature of the ligands in the initiators: P_r = 0.94, 0.88, and 0.80 with respectively trityl (CPh_3), cumyl ($CPhMe_2$), and *tert*-butyl *ortho* substituents on phenolate rings (entries 1, 6, and 8). This dependence of tacticity is consistent with aforementioned observations that ligand substituents are primordial for stereochemical control *via* a chain-end control mechanism.[19,20] At −20 °C, polymerization of *rac*-BBL with complex **2** in toluene proceeded expectedly more slowly, but allowed the formation of a PHB with a higher degree of syndiotacticity (P_r = 0.94, entry 4). Also, to confirm the major influence of the amino-alkoxy-bis(phenolate) ligand on the catalyst performance, a control experiment was carried out with Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ as the initiator (entry 9). The results show that the yttrium complexes **1**−**3** indeed feature significantly higher activity and selectivity than this simple reference system.

Mechanism of the Ring-Opening Polymerization of *rac*-β-Butyrolactone with Aminoalkoxybis(phenolate) Yttrium Initiators. The ring-opening of BBL by metal complexes can proceed by a coordination-insertion mechanism or an anionic mechanism.[5] To investigate the mechanism occurring during the polymerization process, we carried out NMR-scale experiments in THF-d_8. These investigations were conducted with the isopropoxide complex **4**, which is readily obtained *in situ* by reacting the latter complex **2** with 1 equiv of isopropanol and assumed to exist as a mononuclear complex in THF (Scheme 2).[21]

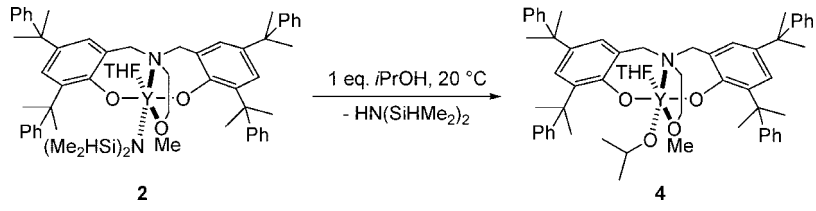
Three ^{1}H NMR spectra were recorded every 30 s over a period of 2 min during the reaction at 20 °C of **2**/*i*PrOH (1:1) with 10 equiv of *rac*-BBL (Figure 1). In the early stage of the reaction (t = 30 s), the spectrum features the −C*H* resonances of unreacted *rac*-BBL and the corresponding oligomers at δ 4.58 ppm and δ 5.20 ppm, respectively. Subsequent spectra show a decrease of the signals for the monomer, while

Table 1. Syndiospecific ROP of *rac*-BBL with Yttrium Complexes[a]

entry	complex	[BBL] /[Y]	[BBL] (mol/L)	time (min)[b]	$M_{n,exp}$[c] (× 10^3 g·mol^{-1})	M_w/M_n[c]	P_r[d]	T_m[e] (°C)
1	**1**	200	2.44	60	27.4	1.03	0.80	133
2	**1**	600	2.44	140	61.2	1.10	0.82	126
3	**2**	400	1.00	10	37.4	1.14	0.90	167
4[f]	**2**	400	1.00	720	37.1	1.10	0.94	178
5	**2**	400	2.44	5	47.2	1.10	0.88	155
6	**2**	600	2.44	5	64.3	1.14	0.88	150
7	**2**	400	4.80	4	36.1	1.08	0.87	150
8	**3**	400	2.44	1	na[g]	na[g]	0.94	183
9	Y[N(SiHMe$_2$)$_3$]$_3$(THF)$_2$	400	2.44	4320	33.0	1.27	0.64	51

[a] All reactions performed at 20 °C until >98% conversion of BBL, unless otherwise stated; results are representative of at least duplicated experiments. [b] Reaction times were not necessarily optimized. [c] Experimental M_n (in g/mol) and M_w/M_n values determined by GPC in THF vs polystyrene standards. [d] P_r is the probability of racemic linkages between monomer units and is determined by ^{13}C{^{1}H} NMR spectroscopy. [e] Determined by DSC. [f] Reaction run at −20 °C. [g] This PHB was not soluble in THF at room temperature and could not be analyzed by GPC.

Scheme 2. *In Situ* Generation of Isopropoxide Complex 4



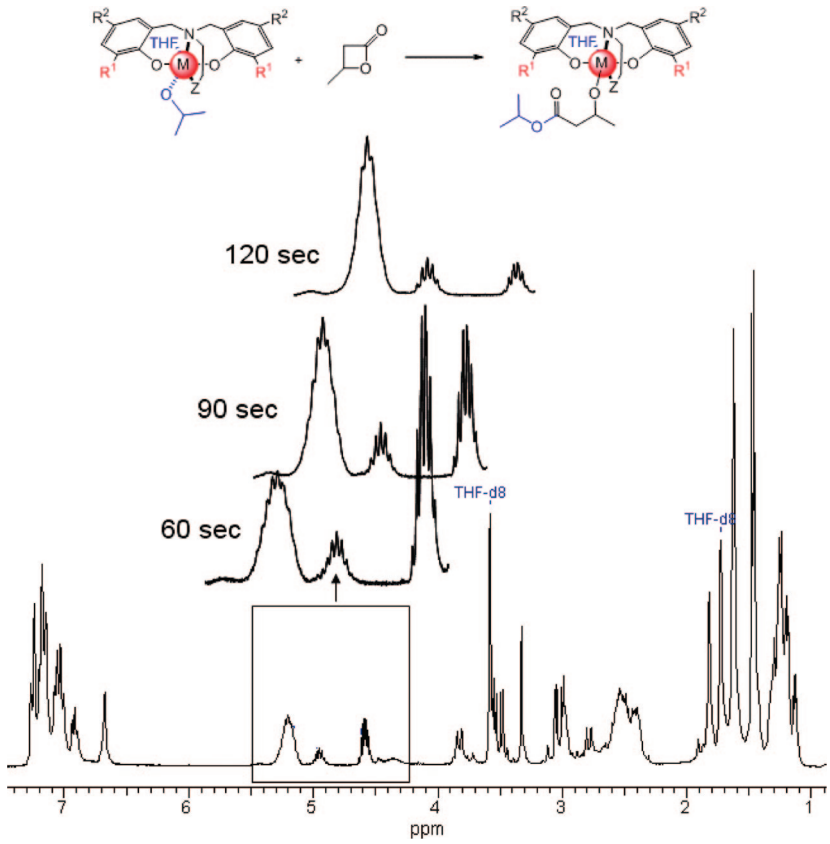
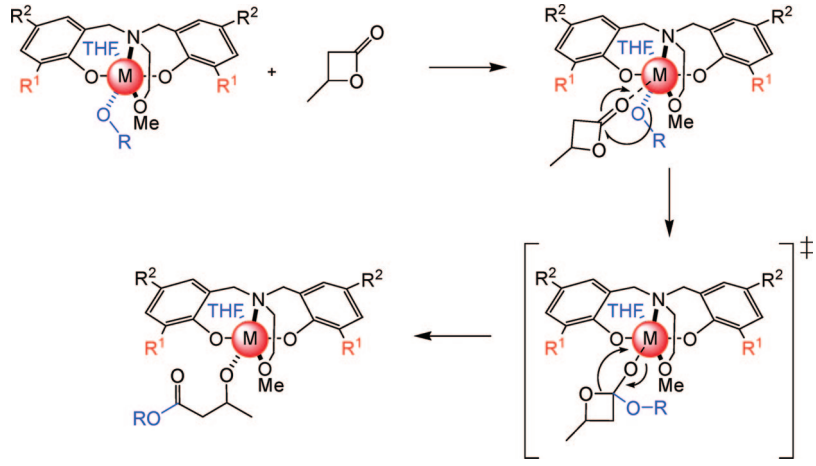


Figure 1. ^{1}H NMR monitoring (500 MHz, THF-d_8, 20 °C) of the reaction of **2**/*i*PrOH (1:1) with 10 equiv of *rac*-BBL.

Scheme 3. Proposed Mechanism for the ROP of BBL by Group 3 Metal Aminoalkoxybis(phenolate) Complexes



the resonance for the methine group in the oligomer increases. After 2 min reaction at 20 °C, 8 equiv of the monomer has been consumed and the corresponding oligomer had formed. The unambiguous identification by ^{1}H NMR spectroscopy of the $-COOCH(CH_3)_2$ end group at δ 4.95 ppm confirmed that the BBL ring is cleaved at the acyl−oxygen bond and inserted into the metal-isopropoxide bond.[18] These *in situ* ^{1}H NMR spectra are in full agreement with the formation of a PHB via a coordination-insertion mechanism, such as summarized in Scheme 3. It is noteworthy that *trans*-crotonate and carboxy groups, which are often observed in the case of an anionic mechanism, were not observed in the ^{1}H NMR spectra of these PHBs, thus corroborating a coordination-insertion mechanism.[15]

Microstructural and Statistical Analysis of Syndiotactic PHBs Produced by the ROP of *rac*-BBL with Aminoalkoxybis(phenolate) Yttrium Initiators. Thanks to the set of PHBs with variable syndiotacticity ($P_r = 0.64-0.94$) synthesized with complexes **1**−**3**, we have been able to run a detailed microstructural analysis by ^{13}C NMR spectroscopy and assign the resonances at the diad and triad level.

Expansion of the methylene region shows four resonances corresponding to triad sensitivity (Figure 2), as shown earlier by Gross et al.[11] The most intense resonance at δ 40.80 ppm was correlated to the (*rr*) triad, and the resonances of equal intensity at δ 40.75 and 40.92 ppm were assigned to the (*mr*) and the (*rm*) triads, respectively.[11,22] The remaining triad at δ 40.88 ppm can be attributed to (*mm*) stereosequences. Note that,

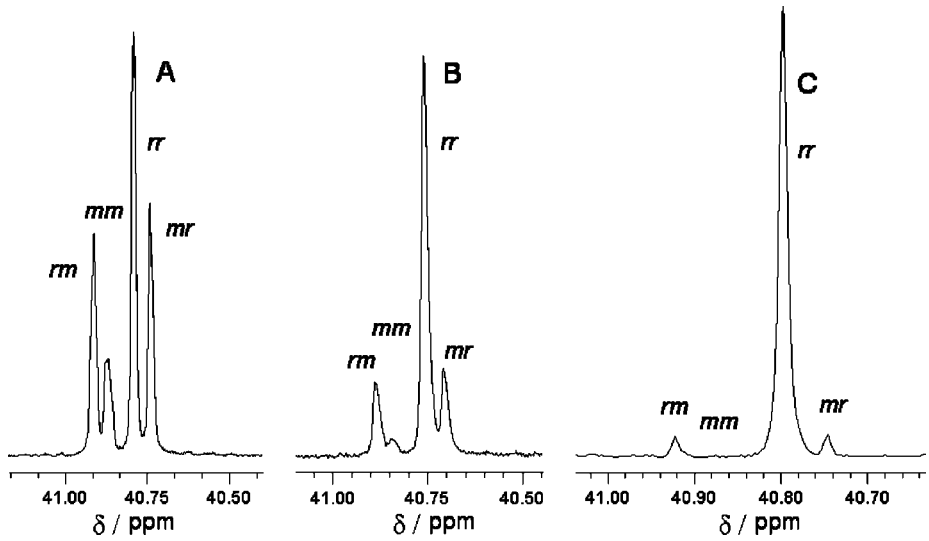


Figure 2. Methylene region of the $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$, 40 °C) of PHBs prepared by ROP of *rac*-BBL. Key: (A) with $Y[N(SiHMe_2)_3]_3(THF)_2$ ($P_r = 0.64$); (B) with complex **1** ($P_r = 0.88$); (C) with complex **3** ($P_r = 0.94$).

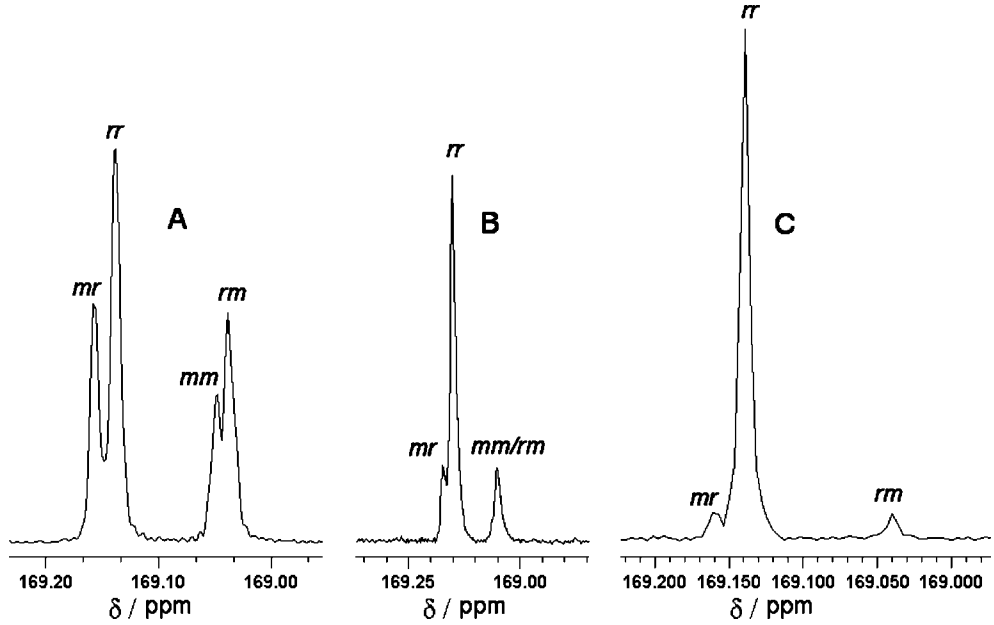


Figure 3. Carbonyl region of the $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$, 40 °C) of PHBs prepared by ROP of *rac*-BBL. Key: (A) with $Y[N(SiHMe_2)_3]_3(THF)_2$ ($P_r = 0.64$); (B) with complex **1** ($P_r = 0.88$); (C) with complex **3** ($P_r = 0.94$).

Table 2. Experimental and Calculated Triad Distributions in the ^{13}C NMR Methylene and Carbonyl Regions of Syndiotactic-Enriched PHBs

		triad distributions												
		experimental values								theoretical values				
		methylene region				carbonyl region								
complex	P_r	(*mr*)	(*rr*)	(*mm*)	(*rm*)	(*mr*)	(*rr*)	(*mm*)	(*rm*)	(*mr*) = (*m*)(*r*)	(*rr*) = (*r*)^2	(*mm*) = (*m*)^2	(*rm*) = (*r*)(*m*)	B^a
1	0.80	0.17	0.610	0.06	0.16	0.17	0.610	0.06	0.16	0.160	0.640	0.04	0.16	1.34
2	0.88	0.101	0.784	0.015	0.100	0.101	0.783	0.015	0.101	0.106	0.774	0.014	0.106	1.16
2^b	0.94	0.063	0.870	0.005	0.063	0.063	0.870	0.005	0.063	0.056	0.884	0.004	0.056	1.10
3	0.94	0.053	0.887	0.004	0.056	0.053	0.890	0.004	0.053	0.056	0.884	0.004	0.056	1.22
Y^c	0.64	0.24	0.380	0.15	0.23	0.23	0.390	0.15	0.23	0.23	0.41	0.13	0.23	1.03

^{a} Bernoulli model triad test *B*, where $B = 4(mm)(rr)/[(rm) + (mr)]^2$. ^{b} Reaction run at −20 °C. ^{c} Y = $[N(SiHMe_2)_3]_3(THF)_2$.

as anticipated, the latter resonance is almost negligible for highly syndiotactic polymers.[23]

Similarly, the carbonyl region shows four peaks that we could assign at the triad level for the first time (Figure 3). As expected, the relative intensities of these resonances are strictly identical to those of resonances in the methylene region for a given PHB sample (Table 2). Thus, we assigned the most intense resonance at δ 169.17 ppm to the (*rr*) triad, the two resonances of equal intensity at δ 169.07 and 169.22 ppm to the (*rm*) and the (*mr*) triads, respectively, and the remaining lower intensity resonance

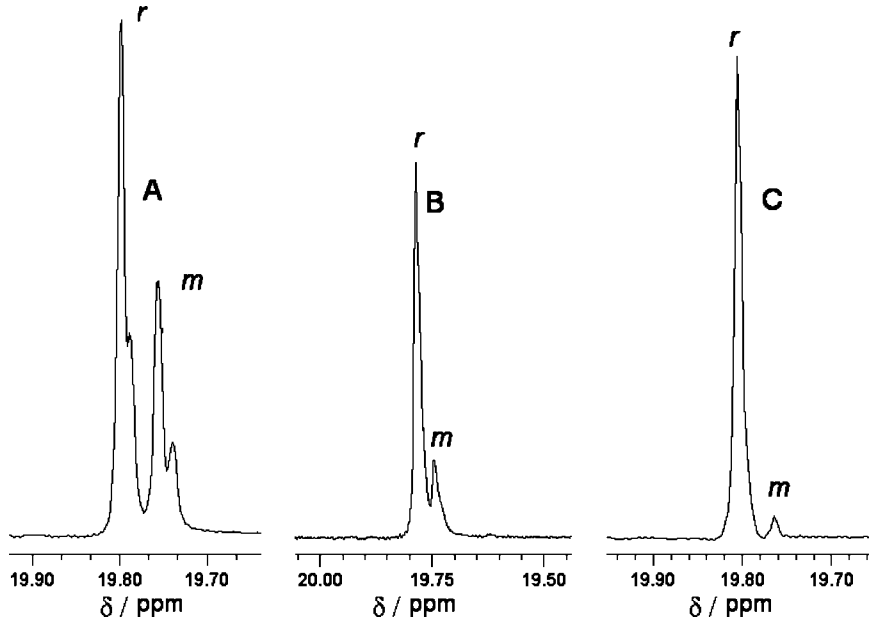


Figure 4. Methyl region of the $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$, 40 °C) of PHBs prepared by ROP of *rac*-BBL. Key: (A) with $Y[N(SiHMe_2)_3]_3(THF)_2$ ($P_r = 0.64$); (B) with complex **1** ($P_r = 0.88$); (C) with complex **3** ($P_r = 0.94$).

Table 3. Thermal Analyses of Syndiotactic-Enriched PHBs Obtained by ROP of *rac*-BBL with Aminoalkoxybis(phenolate) Yttrium Alkoxide Initiators 1−3[a]

complex	M_n (exp)[b] (10^3 g·mol^{-1})	P_r[c]	T_m[d] (°C)	ΔH_m[d] (J·g^{-1})	T_g[d] (°C)	T_g[e] (°C)	T_g[f] (°C)	TGA[g] (°C)
1	61.2	0.82	126	40.4	−3	21.1	27.6	297
2	64.3	0.88	150	53.3	4	22.6	28.8	300
3	na[h]	0.94	183	61.8	11.2	25.3	34.9	294

[a] Results are representative of at least duplicated experiments. [b] Experimental M_n and M_w/M_n values determined by GPC in THF vs polystyrene standards. [c] P_r is the probability of racemic linkages between monomer units and is determined by $^{13}C\{^1H\}$ NMR spectroscopy. [d] T_m, ΔH_m and T_g values determined by DSC. [e] T_g values determined by DMA from the drop in storage modulus (E'). [f] T_g values determined by DMA from tan δ. [g] Temperature for 63% weight loss as determined by TGA. [h] This PHB was not soluble in THF at room temperature and could not be analyzed by GPC; however, as the PHBs in those three entries were prepared under similar conditions (i.e., 600 equiv. BBL vs yttrium), the average number molecular weight of this PHB is assumed to be very similar to those prepared from complexes **1** and **2**.

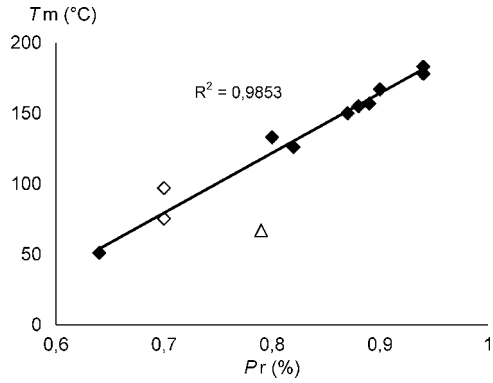


Figure 5. Plot of T_m values vs syndiotacticity degree for PHBs produced via ROP of *rac*-BBL with complexes **1**−**3** and $Y[N(SiHMe_2)_3]_3(THF)_2$ (◆). T_m values of PHBs from other works (◇, ref 11; Δ, ref 25).

at δ 169.09 ppm to the (*mm*) triad. Assignment of the (*rm*) and (*mr*) triad sequences was made assuming a relatively small chemical shift change between (*mm*) and (*rm*), as well as between (*rr*) and (*mr*), since there is a closer spatial proximity of the carbonyl carbon to the repeat unit which is linked to the methylene side of the carboxyl side observed in the stereosequence analysis.

The methyl region shows essentially two peaks that correspond to diad sensitivity (Figure 4); these are actually two groups of resonances, but the limited resolution at 125 MHz does not allow to further discriminate at a higher than diad level. We correlated the most intense group of resonances centered at δ 19.81 ppm to the (*r*) diad, and we attributed the group of resonances centered at δ 19.77 ppm to the (*m*) diad. Integration of these methyl signals led to (*r*) diad fractions (P_r) that are in excellent agreement with those determined at the triad level from the methylene and carbonyl signals (Table 2); i.e., $P_r = 0.64$, 0.88, and 0.94 for $Y[N(SiHMe_2)_3]_3(THF)_2$, and complexes **2** and **3**, respectively.

The methine region of the $^{13}C\{^1H\}$ NMR spectra proved to be more complicated, showing at least six signals (see Supporting Information), evidencing a sensitivity at the tetrad or even higher level. However, due to the insufficient resolution of these resonances at 125.0 MHz, a detailed assignment was not possible.

Statistical Analysis. In addition to information about tacticity, NMR spectroscopy can also provide a great deal of insight into the polymerization mechanism. Two types of stereocontrol mechanisms can operate in ROP of racemic cyclic esters such as *rac*-BBL: an enantiomorphic site control or a chain-end control mechanism. Obviously, due to the use of achiral catalysts, the latter mechanism is likely to be operative in the present systems. Chain-end control is defined in terms of probability of a *racemic* (P_r) or *meso* ($P_m = 1 - P_r$) placement of monomer units and allow to calculate diad/triad/... distributions in terms of Bernoullian analysis.[12,24] In fact, as shown in Table 2, the predicted values for triad distributions compare very well with the experimental values determined by $^{13}C\{^1H\}$ NMR spectroscopy in the methylene and carbonyl regions. Also, the Bernoulli model triad test *B*, where $B = 4(mm)(rr)/[(rm) + (mr)]^2$, ranges from 1.03 to 1.34, which is very close to the theoretical value of 1 for a perfect chain-end control. All those

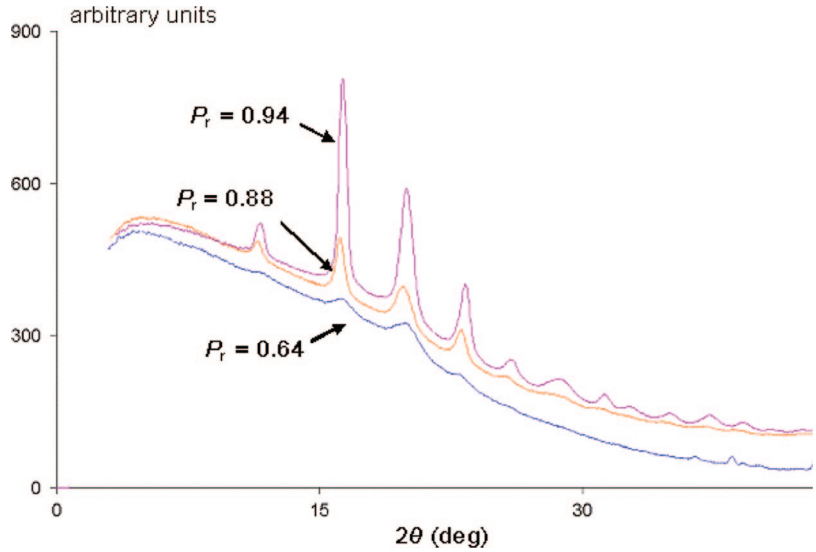


Figure 6. Representative wide-angle X-ray diffraction (WAXD) spectra of PHBs produced via ROP of *rac*-BBL with complexes **1**−**3**.

features unambiguously confirm the anticipated chain-end control tendency of these polymerizations.

Thermal Analyses. We were also interested in evaluating briefly the main thermal properties, i.e., melting temperatures, melting enthalpies and glass transition temperatures, of selected PHB samples to evaluate the influence of the syndiotacticity degree. Representative values are reported in Table 3, and melting temperatures of all prepared PHBs (Table 1) are plotted in Figure 5.

All DSC traces display a single, sharp transition endotherm at high temperature and broad exothermic peak, demonstrating the formation of a uniform crystalline ordering in the solid state (see Supporting Information). The T_m values determined in the present studies increase monotonously and linearly with the syndiotacticity degree (in the range $0.64 < P_r < 0.94$) (Figure 5). Other T_m values reported in earlier studies[11,25] do not all fit perfectly with this relationship (Figure 5). We assume that these discrepancies possibly arise from differences in the molecular weights of PHBs and/or uncertainties or errors in the determination of syndiotacticity degree as well. The melting temperature of the most syndiotactic polymer prepared in this study ($P_r = 0.94$) reaches 183 °C, that is the highest melting temperature reported so far. As can be anticipated, the melting enthalpy (Table 3) and crystallinity (determined by WAXD; Figure 6) of PHBs, also increase significantly with increasing syndiotacticity.

On the other hand, less marked differences were noted in the glass transition temperatures (T_g), determined either by DSC or more accurately by DMA,[26] from the sharp drop in storage modulus, E', and from tan δ (Table 3). These data reveal that (i) the glass transition region extends over a relatively wide temperature range (compare T_g values determined from E' and tan δ peaks) and (ii) the T_g values slightly increase with the syndiotactic degree of PHBs.

Also, the thermal stability of these syndiotactic-enriched PHBs appears rather independent of the syndiotacticity degree (at least in the $0.82 < P_r < 0.94$ range), as revealed by the similar temperatures (294−300 °C) requested for a given (63%) decomposition (Table 3).

Conclusions

Alkoxide- and amidoyttrium(III) complexes supported by tetradendate aminoalkoxybis(phenolate) ligands are efficient initiators for the controlled-living ROP of β-butyrolactone. Fine tuning of the *ortho*-phenolate substituents allows preparing a range of PHBs with a syndiotacticity degree ranging from 80 up to 94%. A detailed microstructural analysis of these polymers allowed a quite complete assignment of $^{13}C\{^1H\}$ NMR spectra and revealed that syndiotacticity originates from a chain-end control. The thermal properties of these PHBs are markedly affected by the syndiotacticity degree. This is especially the case for the melting temperature which raises up to 183 °C for $P_r = 0.94$, a temperature higher than that of pure isotactic PHB (ca. 180 °C). Ongoing studies in this field in our laboratories are directed toward the synthesis of new metal initiators as well as functionalized PHBs for dedicated applications as biomaterials. Results will be reported in due course.

Experimental Section

General Considerations and Analytical Techniques. Complexes **1** and **2** were synthesized as reported.[16] Complex **3** was prepared in an analogous manner.[17] Racemic β-butyrolactone (Aldrich) was freshly distilled from CaH_2 alloy under nitrogen and degassed thoroughly by freeze−thaw−vacuum cycles prior to use.

Size exclusion chromatography (SEC) of PHBs was performed in THF at 20 °C using a Polymer Laboratories PL50 apparatus equipped with PLgel 5 μm MIXED-C 300 × 7.5 mm columns, and combined RI and dual angle LS (PL-LS 45/90°) detectors. The number average molecular masses (M_n) and polydispersity index (M_w/M_n) of the resultant polymers were calculated with reference to a polystyrene calibration.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in 5 mm tubes on a Bruker AC-500 spectrometer operating at 500 and 125 MHz, respectively. The microstructure of PHBs was determined using ca. 0.2 mol.L^{-1} solutions of PHB (reprecipitated with methanol from a dichloromethane solution) in $CDCl_3$ at 40 °C. NMR data acquisition was done with the Bruker pulse program Zgpg and the following parameters: pulse time (P1) = 9.40 μs, relaxation time (D1) = 1.5 s, real transform size (SI) = 64K, and number of scans = 30 000.

DSC analysis of PHBs was carried out on a Mettler-Toledo DSC 822 apparatus, at a heating rate of 10 °C.min^{-1}. First and second runs were recorded after cooling down to ca. −20 °C. The melting temperatures reported in Tables 1 and 3 correspond to second runs.

DMA was carried out on a TA Instruments DMA 2980 apparatus, at a heating rate of 38 °C.min^{-1} in the tension film mode with a deformation amplitude of 10 mm and 1 Hz frequency.

TGA measurements of PHBs were performed under a nitrogen flow using a Setaram TGA 92−12 equipment, at a heating rate of 10 °C.min^{-1}, in the temperature range −20 to 430 °C.

Wide-angle X-ray diffraction (WAXD) was performed at ambient temperature using a X'Pert PRO PANalytical diffractometer. The

X-ray beam was nickel-filtered Cu Kα radiation of wavelength 1.54 Å operated at 35 kV generator voltage and 20 mA current. Diffraction intensity data were collected automatically using a 2θ mode with a step-scanning method (step-widh of 1.07° and 4 s intervals) in the diffraction range of 3−70°.

Typical Polymerization Procedure. In a typical experiment (Table 1, entry 1), in the glovebox, a Schlenk flask was charged with a solution of the initiator **1** (7.0 mg, 8.68 μmol) in toluene (0.70 mL). To this solution was added rapidly β-butyrolactone (150.0 mg, 1.74 mmol, 200 equiv.). The mixture was immediately stirred with a magnetic stir bar at 20 °C for 60 min. After a small sample of the crude material was removed with a pipet for characterization by ^{1}H NMR, the reaction was quenched with acidic methanol (0.5 mL of a 1.2 M HCl solution in MeOH), and the polymer was precipitated with excess methanol (ca. 100 mL). The polymer was then dried under vacuum to constant weight.

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Supporting Information Available: Figures showing additional ^{13}C NMR spectra and DSC, DMA, and TGA traces of PHBs. This material is available free of charge via the Internet at http://pubs.acs.org.

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