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Single-Site β-Diiminate Zinc Catalysts for the Ring-Opening Polymerization of β-Butyrolactone and β-Valerolactone to Poly(3-hydroxyalkanoates)

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Abstract: Polymerization of β-butyrolactone (BBL) and β-valerolactone (BVL) using the zinc alkoxide initiator (BDI-**1**)ZnO^{i}Pr [(BDI-**1**) = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)imino)-2-pentene] proceeds very rapidly under mild conditions to produce poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxyvalerate) (PHV), respectively. For the monomer-to-initiator ratio 200:1, PHB number-average molecular weights (M_n) are proportional to conversion throughout the reaction and polydispersity indices (PDIs) are narrow, consistent with a living polymerization. Higher monomer-to-initiator ratios can be used to achieve high molecular weight PHB (M_n > 100 000). End-group analysis verifies that the polymerization of BBL follows a coordination-insertion mechanism, where complexes of the form (BDI-**1**)ZnOCH(Me)CH$_2$-CO$_2$R are the active species. Variable temperature NMR experiments show that (BDI-**1**)ZnO^{i}Pr is monomeric in benzene-d_6 solution. In contrast, (BDI-**2**)ZnO^{i}Pr [(BDI-**2**) = 2-((2,6-diethylphenyl)amido)-4-((2,6-diethylphenyl)imino)-2-pentene] is a poor initiator at room temperature because it prefers to form a bis-μ-isopropoxide dimer in solution. According to kinetic studies, propagation by (BDI-**1**)ZnO^{i}Pr is first order in both monomer as well as (BDI-**1**)ZnO^{i}Pr concentration. These results lead us to propose a monometallic active species. Several results suggest that elimination side reactions are slowly catalyzed by zinc alkoxides, leading to degradation of the polymer.

Introduction

Poly(3-hydroxybutyrate) (PHB) is an aliphatic polyester produced by bacteria and other living organisms.[1,2] This biodegradable[3−5] and biocompatible[6] natural polymer is isotactic with all stereocenters in the (*R*) configuration. Because isotactic PHB is highly crystalline ($T_m \approx 180$ °C) and has low thermostability, melt processing is difficult, thereby limiting its industrial importance. Recently developed fermentation processes allow other β-hydroxy acids to be incorporated into the polymer, thereby altering the thermomechanical properties of the polymer and improving its processability.[7] In fact, an engineering plastic made from copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), which possesses properties similar to those of polypropylene, has been commercially developed.[1,2,6] However, high production costs of naturally synthesized poly(3-hydroxyalkanoates) (PHAs) render it impractical in many applications.

Ring-opening polymerization (ROP) of β-substituted β-propiolactones offers another approach for producing PHAs. Most efforts to date have focused on the ROP of β-butyrolactone (BBL) to make PHB. Unlike bacteria-mediated polymerization, which gives only isotactic PHB, controlled ROP of BBL allows access to a variety of PHB microstructures. Racemic BBL has been polymerized to make atactic PHB,[8−16] as well as PHB enriched in isotactic[17−20] and syndiotactic[14,21−25] diads. Optically

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pure BBL can also be polymerized to make highly isotactic PHB.[11−14,16,26−28] With the exception of recently reported distannoxane[21,26] and alkylzinc alkoxide[11−13] catalysts, most systems previously studied for the ROP of BBL are extremely slow and/or are not capable of producing high molecular weight PHB (M_n > 100 000) in a controlled manner.

We recently reported that zinc complexes of bulky β-diiminate (BDI) ligands are very active catalysts for the living, stereoselective ROP of lactide to produce poly(lactic acid)[29−31] and living copolymerization of carbon dioxide and epoxides to make polycarbonates.[32−35] Herein, we report that bulky β-diiminate zinc alkoxide complexes are also excellent catalysts for the ROP of BBL and β-valerolactone (BVL). PHAs with narrow polydispersities can be produced at unprecedented rates under mild conditions.

Results and Discussion

Polymerization of *rac*-β-Butyrolactone. Our investigation of the ROP of β-butyrolactone focused on zinc alkoxides (BDI-**1**)ZnO^{i}Pr (**1a**) and (BDI-**2**)ZnO^{i}Pr (**2a**), which are easily prepared in two steps from free BDI ligand (Scheme 1).[29,30] Previous work on the ROP of lactide showed that O^{i}Pr groups on catalyst **1a** directly initiate polymerization at rates competitive with propagation.[29,30] The polymerization of racemic BBL using **1a** and **2a** produces atactic PHB (eq 1); ^{13}C NMR shows equal intensity of racemic and meso diad signals of the carbonyl peak.[36] Results of selected polymerizations are summarized in

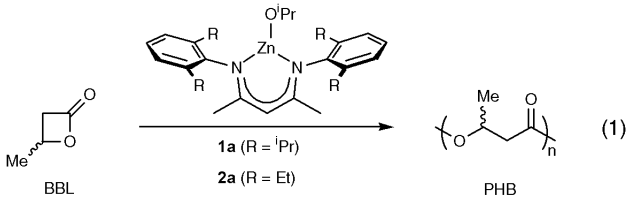

Table 1. When the [BBL]/[Zn] ratio equals 200 (entry 1), polymerization with **1a** surpasses 90% conversion in just over 1 h at room temperature. The number-average molecular weight (M_n) of the polymer (measured by GPC relative to polystyrene standards in THF) grows linearly with conversion and polydispersities (PDIs) are very narrow (Figure 1), suggesting that the polymerization is living. At higher temperatures, polymerizations with **1a** proceed more quickly, as expected. At 50 °C, polymerization at [BBL]/[Zn] = 220 reaches 97% conversion in 20 min (entry 2), while, at 75 °C, the same polymerization reaches 94% conversion in 5 min (entry 3). PDIs remain narrow within all tested temperature ranges.

Molecular weights of the polymer can be increased by altering [BBL]/[Zn] ratios. When [BBL]/[Zn] = 400 (entry 4), polymerization with **1a** yields BBL with M_n = 47 000 at 91% conversion, while, for [BBL]/[Zn] = 1000 (entry 5), M_n = 99 500 at 94% conversion. High molecular weight PHB (M_n > 100 000) is achieved by polymerizing BBL with **1a** at

Scheme 1. Synthesis of (BDI)Zn Alkoxide Complexes

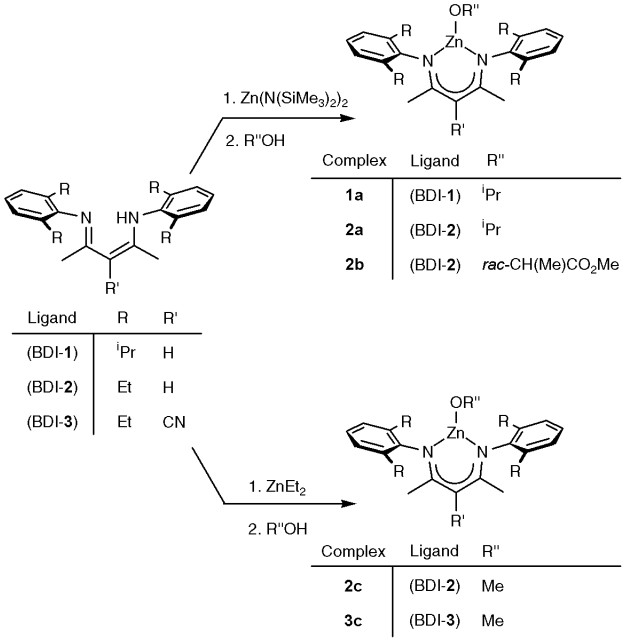

Table 1. Selected Results of Polymerizations of β-Substituted β-Propiolactones with (BDI)Zn Alkoxides[a]

entry	monomer	cat.	M/I[b]	temp (°C)	time (min)	conversion (%)[c]	M_n ($\times 10^{-3}$) (GPC)[d]	M_w/M_n (GPC)[d]
1	*rac*-BBL	**1a**	200	23	70	91	26.1	1.06
2	*rac*-BBL	**1a**	220	50	20	97	29.0	1.10
3	*rac*-BBL	**1a**	220	75	5	94	24.8	1.14
4	*rac*-BBL	**1a**	400	23	150	91	47.0	1.07
5	*rac*-BBL	**1a**	1000	23	480	94	99.5	1.13
6	*rac*-BBL	**1a**	2000	23	720	90	144	1.20
7[e]	*rac*-BBL	**1a**	200	23	70	65	17.1	1.05
8[f]	*rac*-BBL	**1a**	200	23	70	86	23.0	1.08
9	*rac*-BBL	**2a**	200	23	2480	95	200	1.70
10	*rac*-BBL	**2a**	200	50	60	92	48.8	1.30
11	*rac*-BBL	**2a**	200	75	5	94	33.7	1.35
12	*rac*-BBL	**2b**	200	23	70	84	24.7	1.47
13	*rac*-BVL	**1a**	150	23	120	88	12.4	1.15
14	(*R*)-BBL	**1a**	150	23	30	67[g]	9.0	1.04

[a] All polymerizations run in benzene-d_6 except entries 7 (CH_2Cl_2) and 8 (THF); [lactone] = 2.45 M. [b] M/I = [lactone]/[Zn]. [c] As determined by the integration of ^{1}H NMR methine resonances of BBL (or BVL) and PHB (or PHV); polymerizations were quenched with acetic acid-d_4. [d] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [e] Polymerization performed in CH_2Cl_2. [f] Polymerization performed in THF. [g] Polymer precipitates because of insolubility in benzene-d_6.

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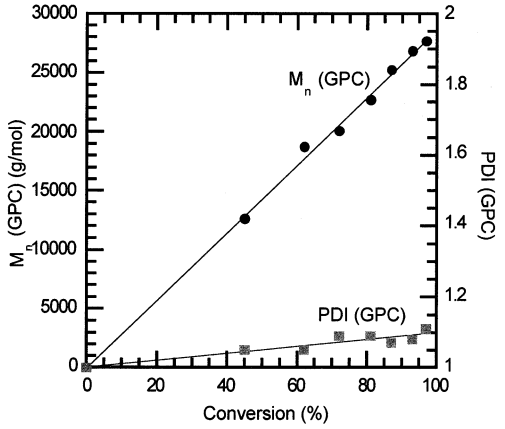


Figure 1. Plot of PHB molecular weight (M_n, GPC vs polystyrene standards) and polydispersity index (PDI) as a function of conversion using *rac*-BBL monomer and (BDI-**1**)ZnO^{i}Pr (**1a**) catalyst ([BBL]$_0$ = 2.45 M, [BBL]/[Zn] = 200).

[BBL]/[Zn] = 2000 at room temperature (entry 6). As [BBL]/[Zn] is increased, however, PDIs broaden and molecular weights are not linearly proportional with [BBL]/[Zn] ratios. For instance, comparing entries 1 and 6 shows that the [BBL]/[Zn] ratio has increased by a factor of 10, but M_n has only increased by a factor of 5.5. Possible explanations for this observation are discussed later (see Side Reactions).[37]

Solvent effects were examined by comparing rates of polymerization by **1a** in benzene-d_6, methylene chloride (CH_2Cl_2), and tetrahydrofuran (THF). At [BBL]/[Zn] = 200, polymerization in benzene-d_6 (entry 1) reached 91% conversion in 70 min, while polymerization in CH_2Cl_2 (entry 7) and THF (entry 8) achieved only 65% and 86% conversion, respectively, in the same time period. As a result, all other polymerizations were conducted in benzene-d_6.

The polymerization of BBL with catalyst **2a** at room temperature produces polymer slowly, requiring over 40 h to reach 95% conversion when [BBL]/[Zn] = 200 (entry 9). In addition, the polymerization with **2a** displays poor control, giving PDI = 1.7 and M_n = 200 000, approximately an order of magnitude higher than the expected M_n. We attribute these results to poor initiation by **2a** at room temperature.

Increasing temperature in polymerizations with **2a** has a dramatic effect. Whereas the room temperature polymerization with **2a** described in the previous paragraph took over 40 h to reach 95% conversion (entry 9), the same polymerization ([BBL]/[Zn] = 200) at 50 °C took only 1 h to reach 92% conversion (entry 10), and at 75 °C, the polymerization reaches 94% conversion in 5 min (entry 11). The molecular weights were much lower (M_n = 48 800 and 33 700, respectively), although still somewhat higher than expected, and the molecular weight distributions were narrower (PDI = 1.30 and 1.35, respectively). These results suggest that initiation is significantly faster at higher temperatures than at room temperature but still slower than propagation.

(37) In general, GPC number-average molecular weights do not correspond well with calculated theoretical molecular weights. In fact, for low [BBL]/[Zn] ratios (e.g., entry 1), GPC molecular weights are somewhat higher than calculated molecular weights, even though initiaton appears to be very fast and efficient for **1a** (see Initiation). We tentatively attribute this mismatch to poor correlation between the polystyrene calibration of the GPC and the actual molecular weights of the PHB chains. However, as the [BBL]/[Zn] ratio increases, GPC molecular weights do not grow proportionately. This could also be partly attributable to the GPC calibration, but there is evidence that side reactions play a role in this unexpected behavior.

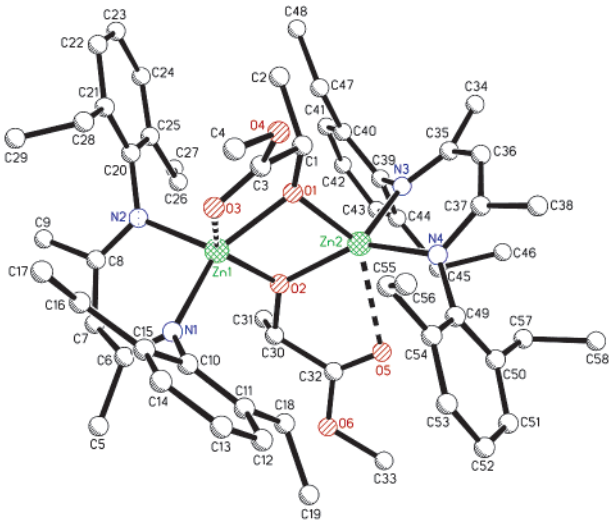


Figure 2. X-ray crystal structure of **2b**. Selected bond distances (Å) and angles (deg): Zn(1)−N(1), 2.022(3); Zn(1)−N(2), 2.019(3); Zn(1)−O(1), 1.971(3); Zn(1)−O(2), 2.052(2); Zn(1)−O(3), 2.459(3); C(1)−O(1), 1.398(4); C(3)−O(3), 1.206(5); O(1)−Zn(1)−N(2), 119.40(1); N(1)−Zn(1)−N(2), 95.59(1); O(1)−Zn(1)−O(2), 76.84(1); N(1)−Zn(1)−O(2), 105.58(1); N(2)−Zn(1)−O(3), 107.73(1); O(1)−Zn(1)−O(3), 72.79(1); Zn(1)−O(1)−Zn(2), 101.29(1); C(1)−O(1)−Zn(1), 124.1(2).

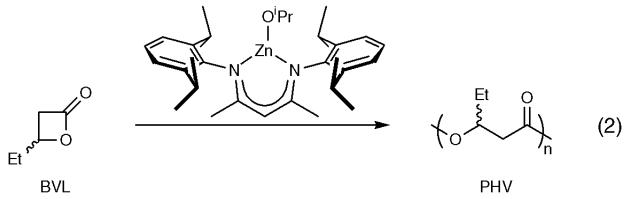
In an attempt to facilitate initiation, we sought to synthesize a (BDI-**2**)Zn alkoxide complex with an initiator that more aptly mimics the putative propagating species. Efforts to prepare (BDI-**2**)ZnOCH(Me)CH_2CO_2Me from a reaction of (BDI-**2**)ZnN(SiMe$_3$)$_2$[29] and methyl 3-hydroxybutyrate failed to generate clean, X-ray quality crystals of the desired product. However, a reaction of (BDI-**2**)ZnN(SiMe$_3$)$_2$ with 1 equiv of racemic methyl lactate yielded (BDI-**2**)ZnOCH(Me)CO_2Me (**2b**) in 48% yield after crystallization. Single-crystal X-ray diffraction revealed that **2b** adopts a dimeric structure in the solid state (Figure 2), in contrast to monomeric (BDI-**1**)ZnOCH(Me)CO_2Me.[29] The five-coordinate zinc center of **2b** exhibits a highly distorted trigonal bipyramidal geometry. Dative bonds are observed between the zinc centers and the carbonyl oxygen of the methyl lactate initiating group. The bond length of Zn(1)−O(3) is 2.46 Å, while the bond angle between O(2)−Zn(1)−O(3) is 139.97°, thus illustrating the distorted geometry around the zinc. The Zn··Zn separation is 3.10 Å, and the six-membered chelate is slightly distorted from planar to a boat-shaped conformation, with a Zn deviation of 0.68 Å from the plane defined by N(1)−N(2)−C(7). The Zn−O bond lengths within the four-membered ring of core atoms are 1.97 and 2.05 Å, and the bond angles of N(1)−Zn(1)−N(2) and O(1)−Zn(1)−O(2) are 95.59° and 76.84°, respectively.

The polymerization of BBL using catalyst **2b** reached 84% conversion after 70 min at room temperature (entry 12). The polydispersity index (PDI = 1.47) is surprisingly broad, but the molecular weight (M_n = 24 700) suggests all Zn complexes participate in the polymerization. Further details about initiation and the solution behaviors of **2a** and **2b** are provided later.

Polymerization of *rac*-β-Valerolactone. β-Valerolactone (BVL), prepared by the carbonylation of 1-butene oxide,[38] is

(38) Getzler, D. Y. L.; Mahadevan, V.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1174−1175.

also polymerized by **1a** to make poly(3-hydroxyvalerate) (PHV) (eq 2). Rates are somewhat slower than those for BBL, requiring

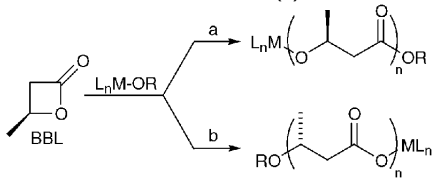


(2)

2 h to polymerize 150 equiv of BVL to 88% conversion at 23 °C (entry 13). Nonetheless, this result suggests that **1a** can be used to produce a variety of copolymers of BBL and BVL.[39] Since it is reasonable to assume that BBL and BVL are polymerized by the same mechanism, the remainder of the paper will focus on the polymerization of BBL.[40]

Mechanism. It is well established that the ring-opening of β-butyrolactone by metal alkoxides can proceed by two mechanisms.[28,41] In a coordination-insertion mechanism, the BBL ring is cleaved at the acyl-oxygen bond. The acid-quenched polymer chains are terminated by ester and hydroxy groups, and the stereochemistry of the chiral center is undisturbed (Scheme 2, path a). In an anionic mechanism, the BBL ring is opened at the alkyl-oxygen bond, leading to carboxylate and ether endgroups, and the methine carbon undergoes inversion (or epimerization) of configuration (Scheme 2, path b).

Scheme 2. Possible Routes for the Ring-Opening Polymerization of β-Butyrolactone (BBL) Using Metal Alkoxide Catalysts: (a) Coordination-Insertion Mechanism and (b) Anionic Mechanism



The polymerization of lactide by **1a** was previously shown to occur by a coordination-insertion route.[29] To confirm that the ROP of β-butyrolactone with **1a** also occurs by a coordination-insertion route, polymerizations of *rac*-BBL were conducted with low [BBL]/[Zn] ratios (e.g., [BBL]/[Zn] $\approx$ 25) ("oligomerization") in order to identify endgroups by ^{1}H NMR. Oligomerizations run for 30 min at room temperature and quenched with acetic acid yielded oligomers with isopropyl ester and hydroxy endgroups, implicating a coordination-insertion mechanism.

In addition, enantiomerically enriched (*R*)-BBL (ee = 95%), prepared by the carbonylation of (*R*)-propylene oxide,[38] was polymerized with **1a** (Table 1, entry 14). As expected, the resulting polymer was shown to be highly isotactic by ^{13}C NMR (Figure 3b) and displays a T_m = 155 °C (versus T_m = 174 °C for commercially supplied natural-origin poly-(*R*)-(3-hydroxybutyrate) with M_n = 540 000). Polarimetry at 365 nm revealed that the polymerization proceeds with retention of the (*R*)-stereocenter,[42] consistent with a coordination-insertion mechanism.

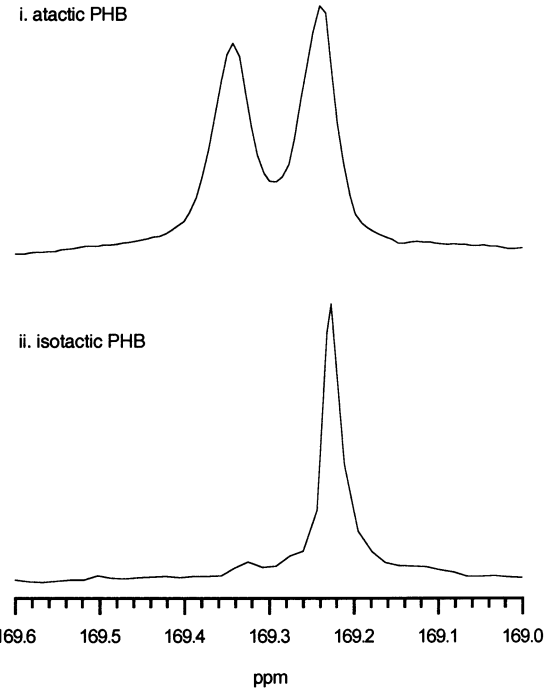


Figure 3. Carbonyl region of the ^{13}C NMR spectra of PHB prepared by the polymerization of (i) *rac*-BBL and (ii) (*R*)-BBL.

Solution Behaviors of (BDI-1)ZnO^{i}Pr and (BDI-2)ZnO^{i}Pr. X-ray crystallography of **1a** and **2a** had previously revealed that both complexes formed bis-μ-isopropoxide dimers in the solid state.[29,30] To establish the nature of the resting-state species in the polymerization of BBL, an understanding of the solution behaviors of **1a** and **2a** is required. Both **1a** and **2a** exhibit only one set of shifts in benzene-d_6 under polymerization conditions (T = 23 °C, and [Zn] $\leq$ 12.3 mM); we sought to elucidate whether the primary species in solution was a monomer or a dimer.

Previous studies had established that (BDI-**2**)ZnOMe[32] (**2c**) exists primarily as a dimer in solution; mixing 1 equiv of (BDI-**2**)ZnOMe with 1 equiv of (BDI-**3**)ZnOMe[43,44] (**3c**), both of which display only one set of shifts by themselves, leads to the formation of a third, mixed ligand species after several days in benzene-d_6 solution.[44] We extended this methodology to show that **2a** also resides primarily in dimeric form in solution. The ^{1}H NMR spectrum of an approximately equimolar solution of

(39) For some recent examples of the copolymerization of β-butyrolactone and β-valerolactone, see: (a) Bloembergen, S.; Holden, D. A.; Bluhm, T. L.; Hamer, G. K.; Marchessault, R. H. *Macromolecules* **1987**, *20*, 3086−3089. (b) Bloembergen, S.; Holden, D. A.; Bluhm, T. L.; Hamer, G. K.; Marchessault, R. H. *Macromolecules* **1989**, *22*, 1663−1669. (c) Kobayashi, T.; Yamaguchi, A.; Hagiwara, T.; Hori, Y. *Polymer* **1995**, *36*, 4707−4710. (d) Noda, I. PCT Int. Appl., WO 0037544, 2000; *Chem. Abstr.* **2000**, *133*, 75001. (e) Noda, I. U.S. Patent 6,077,931, 2000; *Chem. Abstr.* **2000**, *133*, 59245.

(40) A preliminary experiment shows that **1a** also quantitatively polymerizes 2600 equivs of ϵ-caprolactone in less than 1 min at room temperature to produce poly(ϵ-caprolactone) with M_n = 320 000 and PDI = 1.59. We are in the process of optimizing this reaction.

(41) Lavallee, C.; Grenier, D.; Prud'homme, R. E.; Leborgne, A.; Spassky, N. In *Advances in Polymer Synthesis*; Culbertson, B. M., McGrath, J. E., Eds.; Plenum Press: New York, 1985; pp 441−460 and references therein.

(42) The specific rotation at 25 °C in $CHCl_3$ for entry 14 was $[\alpha]^{25}_{365}$ = +8.0 (c = 0.0307 g/mL), compared to $[\alpha]^{25}_{365}$ = +8.3 (c = 0.0252 g/mL) for natural origin (i.e., 100% isotactic) PHB. Both values are lower than literature values ($[\alpha]^{25}_{365} \approx +11$ for natural origin PHB; see: Jedlinski, Z.; Kowalczuk, M.; Kurcok, P.; Adamus, G.; Matuszowicz, A.; Sikorska, W.; Gross, R. A.; Xu, J.; Lenz, R. W. *Macromolecules* **1996**, *29*, 3773−3777). While magnitudes do not precisely correspond to literature values, the fact that entry 14 rotates light in a positive direction indicates that stereochemistry is conserved, while ^{13}C NMR indicates that the degree of isotacticity is very high (>95%).

(43) Coates, G. W.; Cheng, M. PCT Int. Appl., WO 0008088, 2000; *Chem Abstr.* **2000**, *132*, 152332.

(44) Cheng, M. Ph.D. Thesis, Cornell University, 2000.

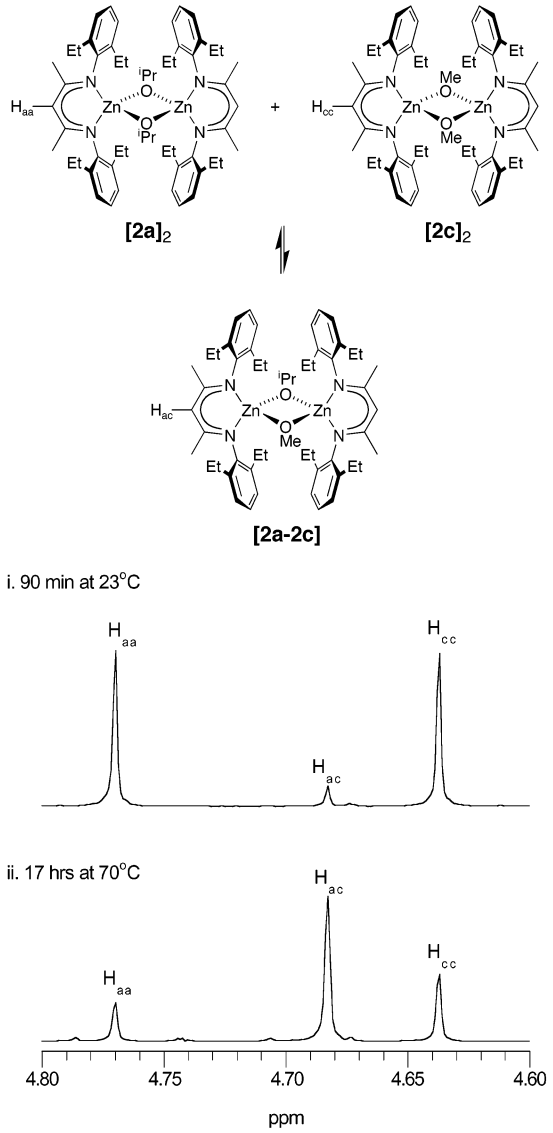


Figure 4. ^{1}H NMR spectra of the β-diiminate methine protons in an equimolar mixture of **2a** and **2c** after (i) 90 min at room temperature and (ii) 17 h at 70 °C. Both spectra show the presence of a third species, the mixed alkoxide dimer [**2a**-**2c**]. The bottom spectrum represents the equilibrium mixture of species.

2a and **2c** in benzene-d_6 ($[Zn]_{tot}$ = 0.056 M) showed the presence of a third species 90 min after mixing at room temperature. After the solution spent an additional 17 h at 70 °C, an equilibrium mixture of the three species had been reached, with roughly the expected 1:2:1 ratio of species observed (Figure 4). The same ratio was observed after another 24 h at 70 °C, allowing us to conclude that equilibrium had been reached.

In contrast, an equimolar mixture of **1a** and **2a** in benzene-d_6 did not give rise to a third species, even after 6 days at 70 °C. This led us to tentatively conclude that **1a** is primarily a *monomer* in solution. Low temperature ^{1}H NMR studies provided compelling further evidence that **1a** resides in a monomeric form in solution. We cooled a concentrated solution of **1a** ([Zn] = 31.7 mM) in toluene-d_8 from 20 °C to 0 °C, recording ^{1}H NMR spectra at 5 °C intervals. At 20 °C, a second species is barely detectable. As temperature is decreased, the second species becomes more prevalent (Figure 5). We attribute the second species to the dimeric form of **1a**. Plotting $\ln(K_{eq})$ versus $1/T$ (van't Hoff plot) for each temperature reveals that $\Delta H° = -18.8 \pm 0.5$ kcal/mol and $\Delta S° = -64 \pm 2$ eu for the monomer−dimer equilibrium (Figure 6).[45] Under normal po-

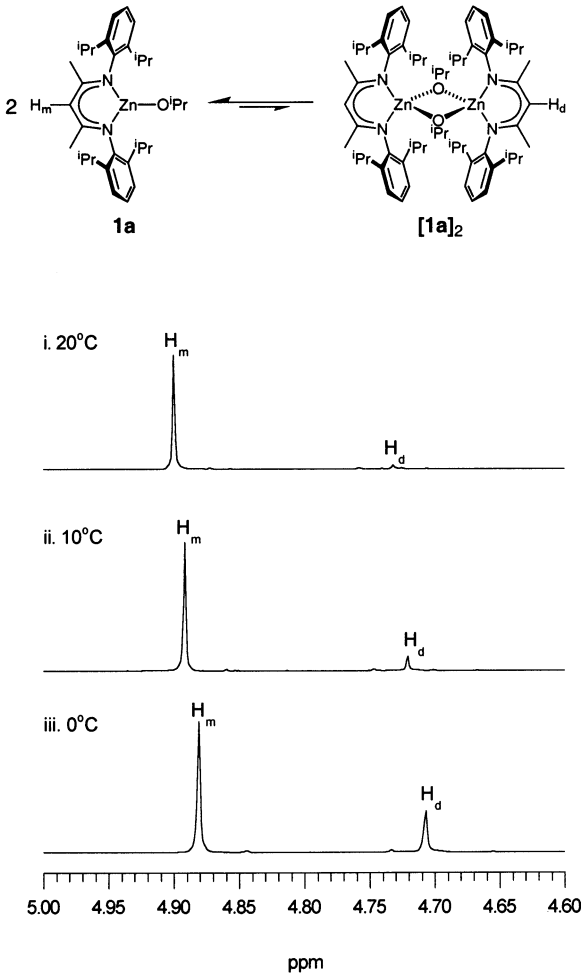


Figure 5. ^{1}H NMR spectra of the β-diiminate methine proton of **1a** ([Zn] = 31.7 mM in toluene-d_8) at (i) 20 °C, (ii) 10 °C, and (iii) 0 °C.

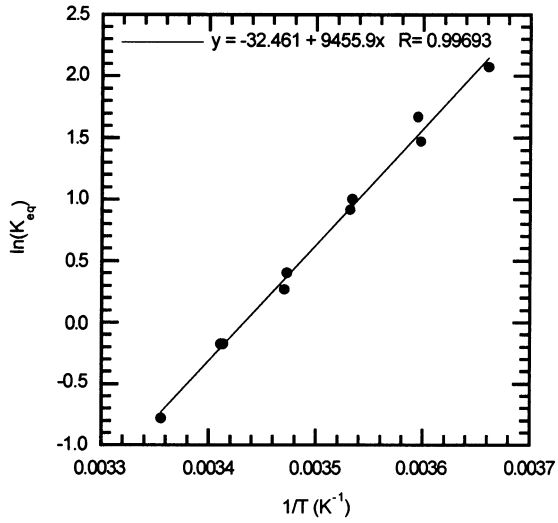


Figure 6. van't Hoff plot for the monomer−dimer equilibrium of **1a** in toluene-d_8 ([Zn] = 31.7 mM).

(45) The variable temperature NMR data described in the text were combined with an additional set of spectra recorded at 5 °C intervals from 25 °C to 5 °C with the same sample.

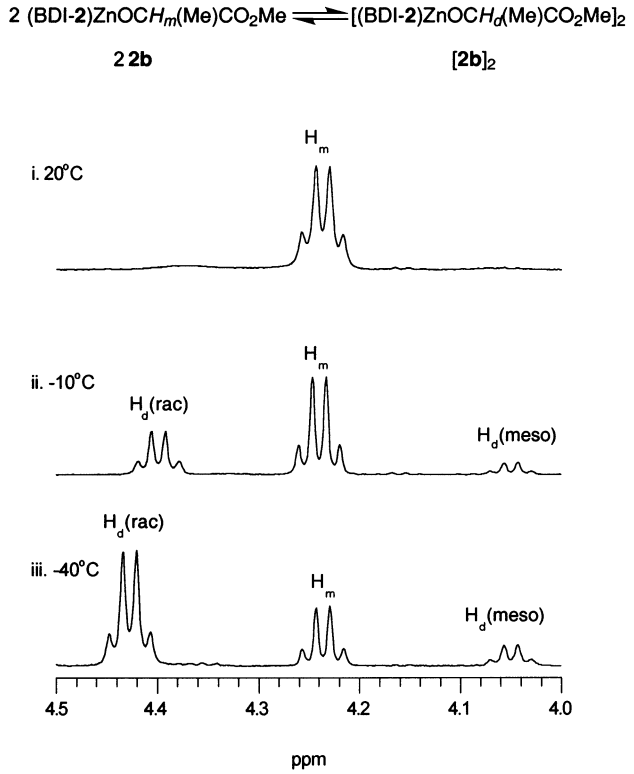


Figure 7. ^{1}H NMR spectra of the methyl lactate methine proton of **2b** ([Zn] = 58.0 mM in toluene-d_8) at (i) 20 °C, (ii) −10 °C, and (iii) −40 °C.

lymerization conditions, **1a** resides almost exclusively in monomeric form.

Similar variable temperature experiments with **2a** failed to reveal a second species despite looking at a wide range of temperatures and concentrations. Nonetheless, the mixed ligand experiments described above strongly suggest **2a** prefers a dimeric form under polymerization conditions.

Variable temperature ^{1}H NMR experiments with **2b** in toluene-d_8 revealed that it, like **1a**, resides primarily as a monomer in solution under polymerization conditions (12.3 mM, 23 °C) despite forming a bis-μ-alkoxide dimer in the solid state (Figure 2). A 58.0-mM solution of **2b** in toluene-d_8 was cooled from 20 °C to −40 °C in 10 °C intervals. The ^{1}H NMR peaks corresponding to the methine protons of the methyl lactate initiator are shown in Figure 7. Only one species is visible at 20 °C; we believe this species is a monomeric complex in which the methyl lactate carbonyl oxygen is coordinated to the zinc center. As the solution is cooled, however, *two* new peaks become visible. We attribute these two peaks to the meso and racemic forms of the bis-μ-alkoxide dimer, with the larger peak corresponding to the *rac*-dimer. This assignment was corroborated by resynthesizing (BDI-**2**)ZnOCH(Me)CO_2Me with (*S*)-methyl lactate; low temperature ^{1}H NMR revealed that, in this case, only one additional peak, corresponding to (*S*,*S*)-[(BDI-**2**)ZnOCH(Me)CO_2Me]$_2$, grew in at 4.4 ppm as temperature was reduced.

By adding the intensities of the two dimer peaks for **2b**, we calculated K_{eq} for the monomer−dimer equilibrium at each temperature. In this case, plotting ln(K_{eq}) versus 1/T for the temperature range 0 °C to −40 °C gave $\Delta H° = -9.6 \pm 0.1$ kcal/mol and $\Delta S° = -32.2 \pm 0.3$ eu for the monomer−dimer equilibrium (Figure 8).

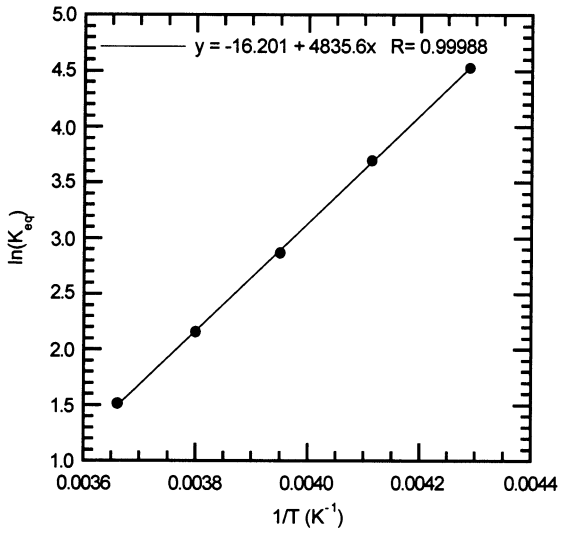


Figure 8. van't Hoff plot for the monomer−dimer equilibrium of **2b** in toluene-d_8 ([Zn] = 58.0 mM).

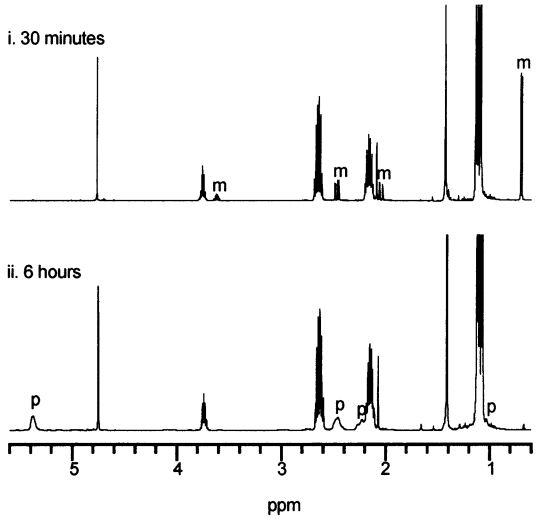
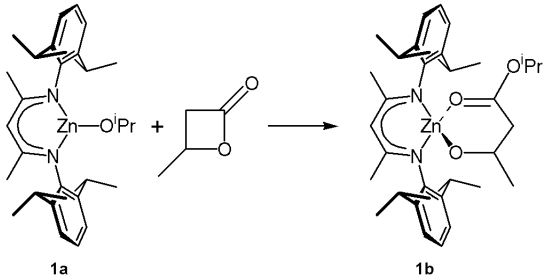


Figure 9. ^{1}H NMR spectra of the reaction of **2a** with 1 equiv of BBL after (i) 30 min and (ii) 6 h. After 30 min, only BBL (m) and unreacted **2a** are observed. After 6 h, a vast majority of unreacted **2a** remains, but BBL has been replaced with PHB (p).

Scheme 3. Reaction of (BDI-**1**)ZnO^{i}Pr (**1a**) with 1 Equiv of BBL Yields Monoinsertion Product (BDI-**1**)ZnOCH(Me)$CH_2CO_2{}^i$Pr (**1b**)



Initiation. To compare initiation rates of **1a** and **2a**, we ran NMR-scale reactions of the Zn catalysts with 1 equiv of BBL at room temperature. For **1a**, the ^{1}H NMR spectrum taken 15 min after the reagents were combined revealed that all the BBL had been consumed, and the monoinsertion product **1b** (Scheme 3) had formed exclusively; that is, peaks corresponding to the polymer were not observed. This suggests that, for **1a**, the rate of initiation is greater than the rate of propagation. In contrast,

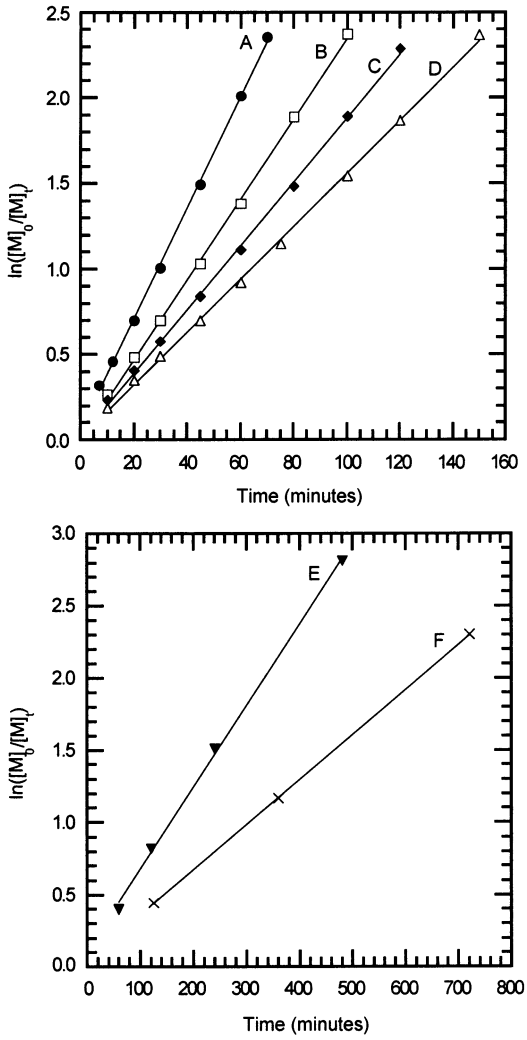


Figure 10. First-order kinetic plots for the polymerization of BBL with (BDI-**1**)ZnO^{i}Pr (**1a**) as initiator ([BBL]$_0$ = 2.45 M: (A) [BBL]/[Zn] = 100; (B) [BBL]/[Zn] = 150; (C) [BBL]/[Zn] = 200; (D) [BBL]/[Zn] = 250; (E) [BBL]/[Zn] = 1000; (F) [BBL]/[Zn] = 2000).

the ^{1}H NMR spectrum taken 30 min after **2a** and 1 equiv of BBL were combined revealed primarily unreacted **2a** and BBL. After 6 h, the BBL had been consumed. But, a vast majority of **2a** remained and polymer had formed (Figure 9). This experiment suggests that initiation by **2a** is extremely slow at room temperature, and only a small percentage of **2a** participates in the polymerization.

Kinetics. A kinetic study was conducted in order to establish reaction order in monomer and zinc for the polymerization of BBL with **1a**. Conversion of *rac*-BBL was monitored by ^{1}H NMR for various catalyst concentrations at room temperature ([BBL]/[Zn] = 200−2000; [BBL] = 2.45 M in benzene-d_6). In each case, polymerization proceeds with first-order dependence on monomer concentration (Figure 10). Thus, the rate of polymerization can be written as

$$-\mathrm{d[BBL]/dt} = k_{app}[\mathrm{BBL}]$$

where $k_{app} = k_p[\mathrm{Zn}]^x$. Plotting ln k_{app} versus ln[Zn] allows us to determine x, the order in Zn concentration, from the slope of the fitted line (Figure 11). On the basis of this analysis, x = 1.02 ± 0.02.[46] Thus, the reaction is first order in zinc and monomer concentrations, and the overall rate equation is

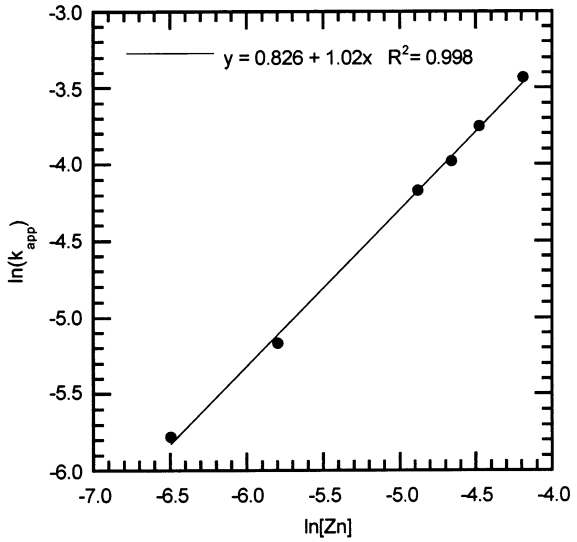


Figure 11. Plot of ln k_{app} versus ln[Zn] for the polymerization of BBL with (BDI-**1**)ZnO^{i}Pr (**1a**) as initiator ([BBL]$_0$ = 2.45 M).

$$-\mathrm{d[BBL]/dt} = k_p[\mathrm{BBL}][\mathrm{Zn}]$$

Since we established that **1a** remains monomeric under polymerization conditions and can reasonably assume that the zinc complex of the growing polymer chain is also monomeric, an order in [Zn] = 1 suggests that the ROP of BBL proceeds through a monometallic transition state in the rate-determining step. We thus propose the polymerization mechanism shown in Scheme 4: the BBL monomer coordinates to the Zn center of the monometallic complex; the alkoxide chain end attacks the activated carbonyl carbon, cleaving the acyl−oxygen bond and producing a new alkoxide chain end.

Complex **2a** is a poor initiator for the ROP of BBL at room temperature because it prefers to adopt the inactive dimeric form, which inhibits coordination of the monomer and, therefore, prevents polymerization. This limitation is minimized by using higher temperature, which pushes the monomer−dimer equilibrium toward the active monomer, or by using a "preinitiated" Zn complex like **2b**. Once an insertion has occurred, propagation can proceed readily.

Side Reactions. As Table 2 indicates, PHB slowly degrades under polymerization conditions after monomer has been consumed. When BBL is polymerized by **1a** to 99% conversion at 23 °C, PDIs are still very narrow (entry 1). However, if the reaction is allowed to continue for an additional 20 h at 23 °C (entry 2) or is heated to 50 °C for 2 h (entry 3), the PDIs of the polymer broaden and molecular weights decrease. In addition, we have already noted that molecular weights of PHB synthesized at different [BBL]/[Zn] ratios do not correlate well with calculated theoretical molecular weights; as [BBL]/[Zn] is increased, M_n(GPC) does not grow proportionally. Previous investigations of lactone polymerization by metal alkoxides have reported similar behavior.[47−50] The most common explanation for these observations has been transesterification and elimina-

(46) Interestingly, we had previously found an order in [Zn] of 1.56 for the polymerization of *rac*-lactide by **1a**; see ref 29. We are currently seeking to understand the reason we obtained a higher order in catalyst for a seemingly similar polymerization.

Scheme 4. Proposed Mechanism for the ROP of BBL by (BDI)ZnOR′ Catalysts

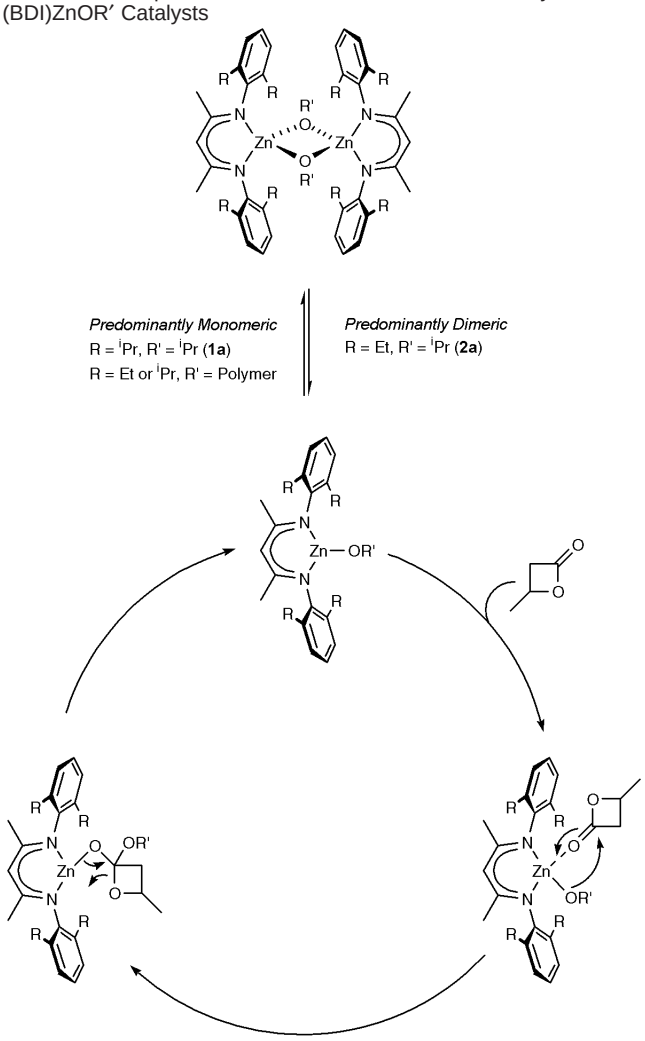


Table 2. Polydispersity Broadening and Molecular Weight Reduction after Monomer Consumption in Polymerizations of *rac*-BBL with (BDI-**1**)ZnO*i*Pr (**1a**)[a]

entry	cat.	M/I[b]	temp (°C)	time (min)	conversion[c] (%)	M_n ($\times 10^{-3}$) (GPC)[d]	M_w/M_n (GPC)[d]
1	**1a**	200	23	90	99	27.6	1.09
2	**1a**	200	23	1200	100	25.3	1.20
3	**1a**	200	23/50	90/130	100	24.6	1.21

[a] Polymerizations run in benzene-d_6; [BBL] = 2.45 M. [b] M/I = [BBL]/[Zn]. [c] As determined by the integration of ^{1}H NMR methine resonances of BBL and PHB; polymerizations were quenched with acetic acid-d_4. [d] Determined by gel permeation chromatography calibrated with polystyrene standards in THF.

tion reactions promoted by the metal complex. Various zinc,[13] aluminum,[49] and tin[10,50] alkoxide catalysts for the ROP of β-butyrolactone have been reported to catalyze transesterification. In addition, Jérôme and co-workers noted the presence of crotonate groups in PHB prepared by the ROP of BBL with $Al(O^iPr)_3$; they proposed that the metal catalyst promotes elimination, which leads to chain cleavage and formation of

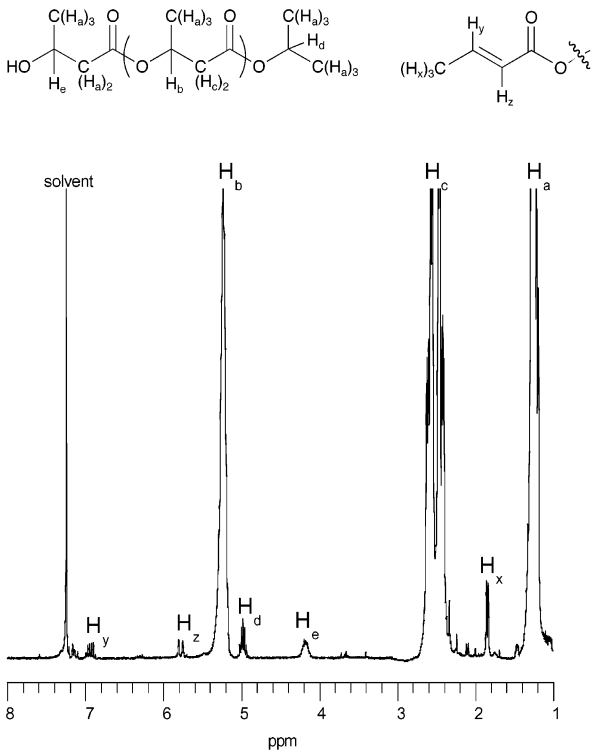


Figure 12. ^{1}H NMR spectrum of the product of the oligomerization of BBL ([BBL]/[Zn] = 25) by **1a** for 20 h at room temperature (after acidic quench).

crotonate (and carboxy) endgroups.[49] Tin-based catalysts have also been shown to catalyze elimination.[48,51,52]

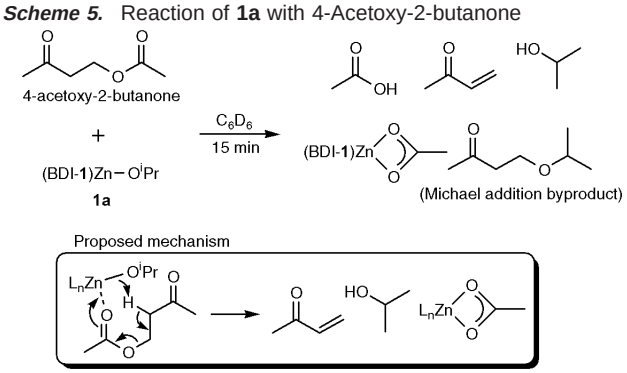
^{1}H NMR studies of oligomerization reactions revealed that **1a** also promotes the elimination reaction. As mentioned above, oligomerizations run at room temperature for 30 min yield oligomers with only isopropyl ester and hydroxy endgroups. However, if the oligomerization is run at elevated temperature (e.g., 75 °C) or for extended periods (e.g., 20 h), peaks consistent with *trans*-crotonate groups are also observed in the ^{1}H NMR (Figure 12).

To further investigate the effect of **1a** on the elimination reaction, we stirred 62 mg of commercially supplied natural-origin poly-(*R*)-(3-hydroxybutyrate) ((*R*)-PHB) with 24.2 mg of catalyst **1a** (PHB repeat unit/Zn = 16) in $CHCl_3$ for 2 h at 50 °C. The proton NMR spectrum of the resulting product clearly showed the presence of crotonate peaks, and GPC revealed that the average molecular weight of the polymer had been reduced from 540 000 to less than 5000.[53] In contrast, (*R*)-PHB stirred in $CHCl_3$ at 50 °C *without* catalyst for 20 h displayed no crotonate groups by NMR. This result, coupled with the fact that this polymer remained insoluble in THF, led us to conclude that elimination is minimal in the absence of **1a**.

The ability of **1a** to promote elimination reactions was further demonstrated by treating **1a** with 1 equiv of model compound

(47) Dubois, P.; Jacobs, C.; Jérôme, R.; Teyssié, P. *Macromolecules* **1991**, *24*, 2266−2270.
(48) Kricheldorf, H. R.; Scharnagl, N.; Jedlinski, Z. *Polymer* **1996**, *37*, 1405−1411.
(49) Kurcok, P.; Dubois, P.; Jérôme, R. *Polym. Int.* **1996**, *41*, 479−485.
(50) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286−293.
(51) Melchiors, M.; Keul, H.; Höcker, H. *Macromol. Rapid Commun.* **1994**, *15*, 497−506.
(52) Melchiors, M.; Keul, H.; Höcker, H. *Macromolecules* **1996**, *29*, 6442−6451.
(53) The commercially prepared PHB was not soluble in THF, the eluent for our GPC instrument. Molecular weight data were supplied by Fluka, M_n = 540 000, but no polydispersity data were available. Stirring the commercial polymer with **1a** in $CHCl_3$, as described, reduced the molecular weight enough such that the resulting polymer was soluble in THF (M_n = 4160, PDI = 1.60). Integrating the crotonate methyl groups in the ^{1}H NMR spectrum versus the PHB methyl gives M_n = 4300.

Scheme 5. Reaction of **1a** with 4-Acetoxy-2-butanone



4-acetoxy-2-butanone in benzene-d_6. After 30 min, the reaction solution was split into volatile and nonvolatile fractions by vacuum transfer. ^{1}H NMR analysis of the nonvolatile fraction revealed complete transformation of the zinc species **1a** to (BDI-**1**)ZnOAc;[33] a small amount of protonated ligand was also observed. In the volatile fraction, the 4-acetoxy-2-butanone was largely consumed, yielding the expected elimination products 2-propanol and methyl vinyl ketone, plus acetic acid and a small amount of Michael addition product 4-isopropoxy-2-butanone (Scheme 5). This experiment provides indirect evidence that **1a** induces the elimination reaction on the PHB backbone.

The role of transesterification in polymerizations of BBL with **1a** is more difficult to assess. Interestingly, when commercially prepared poly-(*R*)-(3-hydroxybutyrate) ((*R*)-PHB) was stirred for 2 h with catalyst **1a** in $CHCl_3$ at 50 °C (see above), GPC peaks consistent with low molecular weight PHB cyclics were *not* observed in the decomposition product, suggesting that intramolecular transesterification (backbiting) is negligible compared with elimination under these conditions. In fact, we have found little evidence that transesterification is prominent in this system, on the basis of the narrow PDIs and lack of low MW cyclics in reaction products, even at 75 °C. Furthermore, despite the evidence that elimination is facilitated by **1a**, we cannot rule out the possibility that the nonliving behavior we observed is due to the presence of impurities in the monomer, since the nonliving behavior is more pronounced at high [BBL]/[Zn] ratios and BBL is notoriously difficult to prepare in >99.9% purity.

Conclusions

Zinc alkoxide complex **1a** is an easily synthesized and extremely efficient catalyst for the ring-opening polymerization of strained lactones. We had previously reported that β-diiminate zinc alkoxides are extremely active catalysts for the living, stereoselective ROP of lactide.[29,30] In this paper, we demonstrate that **1a** polymerizes BBL and BVL with unprecedented rates under mild conditions to make PHAs in a controlled manner.

Prior to this report, the active form of the β-diiminate zinc species for ROP of lactones was largely unresolved.[29] The experimental results described in this paper strongly suggest that a *monometallic* zinc complex mediates the insertion of the β-butyrolactone monomer at the alkoxide chain end. Ring opening occurs with acyl−oxygen bond cleavage and, therefore, retention of configuration at the chiral methine carbon. We believe this model can be extended to describe the behavior of **1a** in other lactone polymerizations; we are currently investigating this hypothesis.

The results presented in this paper bring us a step closer to an alternative route for making poly(3-hydroxyalkanoates). Despite a host of potential applications, PHAs produced by bacterial fermentation and other natural processes remain too expensive for widespread use. The carbonylation of epoxides to make optically pure β-substituted β-propiolactones[38] followed by the polymerization of the β-substituted β-propiolactones using (BDI)Zn alkoxides represents an efficient route to PHAs from abundant feedstocks.

Experimental Section

General Considerations. All reactions with air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun Labmaster drybox or standard Schlenk line techniques. NMR spectra were recorded on a Bruker AF300 (^{1}H, 300 MHz; ^{13}C, 75 MHz), Varian VXR-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), or Varian Unity 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer and referenced versus residual solvent shifts. Gel permeation chromatography (GPC) analyses were carried out using a Waters instrument (M510 pump, U6K injector) equipped with Waters UV486 and Waters 2410 differential refractive index detectors and three 5-mm PL gel columns (Polymer Laboratories; 100, 500, and 1000 Å) in series. The GPC columns were eluted with tetrahydrofuran at 40 °C at 1 mL/min and were calibrated using a polynomial fit to 10 monodisperse polystyrene standards. Optical rotation experiments were conducted in chloroform at 25 °C using a Perkin-Elmer 241 polarimeter. DSC analyses were conducted on a Seiko DSC 220C instrument using EXSTAR 6000 processing software. The measurements were made in aluminum crimped pans under nitrogen with a heating rate of 10 °C/min.

Materials. Benzene-d_6, toluene-d_8, and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen and degassed by three freeze-pump-thaw cycles. Benzene-d_6 and toluene-d_8 were stored over activated 4 Å molecular sieves. Methylene chloride was collected from activated alumina-packed solvent columns and degassed by three freeze-pump-thaw cycles. Chloroform was distilled from phosphorus pentoxide under nitrogen and degassed by three freeze-pump-thaw cycles. Racemic β-butyrolactone was purchased from Aldrich, while (*R*)-β-butyrolactone and β-valerolactone were prepared according to published procedures.[38] β-Butyrolactone was dried with CaH_2 for 3 days, vacuum transferred onto activated 4 Å molecular sieves, and then fractionally distilled under reduced pressure; the entire process was then repeated. Note: β-butyrolactone is a suspected carcinogen; thus, it should be handled with appropriate safeguards. β-Valerolactone was dried with CaH_2 for 3 days, vacuum transferred onto activated 4 Å molecular sieves, and then fractionally distilled under reduced pressure. Complexes **1a**, **2a**, **2c**, and (BDI-**2**)ZnN(SiMe$_3$) were prepared according to published procedures.[29,30,32] Poly-(*R*)-(3-hydroxybutyrate) was purchased from Fluka and dried under vacuum for 1 h prior to use.

***rac*-(BDI-2)ZnOCH(Me)CO$_2$Me (2b).** To a solution of (BDI-**2**)-ZnN(SiMe$_3$)$_2$[29] (1.45 g, 2.47 mmol) in toluene (5 mL) was added racemic methyl lactate (0.24 mL, 2.5 mmol). After the clear yellow solution was stirred at room temperature for 6 h, it was dried in vacuo. The resulting white powder was dissolved in hexanes (20 mL) and filtered through a pad of Celite. The filtrate was concentrated and cooled to −30 °C; whereupon, *rac*-(BDI-**2**)ZnOCH(CH$_3$)CO$_2$Me (**2b**) crystallized as colorless blocks (0.636 g, 48% yield). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.07 (6H, m, Ar*H*), 4.88 (1H, s, β-C*H*), 4.24 (1H, quartet, J = 7 Hz, OC*H*(Me)CO$_2$CHMe$_2$), 3.00 (3H, s, CO$_2$*Me*), 2.90 (2H, m, J = 7 Hz, ArC*H*$_2$Me), 2.85 (2H, m, J = 7 Hz, ArC*H*$_2$Me), 2.64 (4H, m, J = 7 Hz, ArC*H*$_2$Me), 1.64 (6H, s, α-Me), 1.25 (12H, m, ArCH$_2$*Me*), 0.73 (3H, d, J = 7 Hz, OCH(*Me*)CO$_2$CHMe$_2$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100 MHz): δ 192.56, 168.75, 146.72, 138.02, 137.92, 126.31, 125.58, 94.27, 70.91, 53.14, 24.73, 24.00, 23.65, 14.70 ppm. X-ray analysis of the crystals revealed that the complex exists as a μ-alkoxide-bridged dimer in the solid state (see Supporting Information).

(*R*)-(BDI-1)ZnOCH(CH$_3$)CH$_2$CO$_2$^{i}Pr (1b). To a solution of (BDI-**1**)ZnO^{i}Pr (**1a**) (0.124 g, 0.229 mmol) in toluene (3 mL) was added a 1.227 M solution of (*R*)-*β*-butyrolactone in C_6D_6 (0.19 mL, 0.23 mmol). After the clear colorless solution was stirred at room temperature for 15 min, it was dried in vacuo to yield a white powder. Despite repeated attempts, efforts to grow X-ray-quality crystals of the complex were unsuccessful. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.14 (6H, m, Ar*H*), 4.92 (1H, s, *β*-C*H*), 4.82 (1H, m, OCH(Me)CH$_2$CO$_2$C*H*Me$_2$), 4.14 (1H, m, OC*H*(Me)CH$_2$CO$_2$CHMe$_2$), 3.55 (4H, m, ArC*H*Me$_2$), 1.80 (1H, dd, J = 14 Hz and J = 3 Hz, OCH(Me)C*H*$_2$CO$_2$CHMe$_2$), 1.77 (6H, s, α-Me), 1.62 (1H, dd, J = 14 Hz and J = 7 Hz, OCH(Me)C*H*$_2$CO$_2$CHMe$_2$), 1.42 (12H, d, J = 7 Hz, ArCH*Me*$_2$), 1.22 (12H, d, J = 7 Hz, ArCH*Me*$_2$), 1.00 (3H, d, J = 6 Hz, OCH(*Me*)CH$_2$CO$_2$CHMe$_2$), 0.81 (3H, d, J = 6 Hz, OCH(Me)CH$_2$CO$_2$CH*Me*$_2$), 0.80 (3H, d, J = 6 Hz, OCH(Me)CH$_2$CO$_2$CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 169.49, 145.05, 142.93, 125.61, 123.84, 123.81, 93.93, 69.45, 67.48, 47.09, 28.26, 28.16, 24.78, 24.72, 24.67, 24.62, 23.84, 21.64, 21.55 ppm (one resonance missing, possibly because of resolution or chemical shift equivalence).

General Polymerization Procedure. In the glovebox, the catalyst was dissolved in 1.0 mL of solvent in a small vial. *β*-Butyrolactone (0.25 mL) was added to the vial, and the reaction solution was transferred to a Teflon-sealed NMR tube. The reaction solution was quickly removed from the glovebox and inserted into a temperature-controlled NMR. Conversion was monitored by comparing the relative magnitude of peaks corresponding to the methine hydrogen for BBL and PHB. Polymerizations were quenched by adding five drops of acetic acid-d_4. The resulting solution was filtered over a Celite/glass wool plug 1 h after quenching. The polymer was isolated by removing solvent in vacuo.

When nondeuterated solvents were used, the polymerization solution was sealed in a small vial with a Teflon cap. Temperature was controlled using an oil bath (except at room temperature). Conversion was measured after the polymerization was quenched with five drops of acetic acid-d_4 by ^{1}H NMR of an aliquot of the quenched reaction solution in benzene-d_6.

Reaction times for polymerizations conducted at room temperature reflect the time between the addition of BBL to the catalyst solution and the quenching of the reaction; in contrast, the start time for polymerizations conducted at 50 °C or 75 °C corresponds to the time the reaction solution is introduced to the heat source (i.e., NMR or oil bath), which is generally 2−3 min after the addition of BBL to the catalyst solution.

To further purify the polymer for endgroup analysis, the polymer was redissolved in chloroform; several drops of 1% HCl (in MeOH) solution were added, and the solution was again filtered over Celite. The polymer was precipitated by the addition of hexanes; the mother liquor was removed by decanting, and the polymer was dried in vacuo. Polymer samples were precipitated *twice* from chloroform with hexanes (to remove residual ligand) prior to polarimetry experiments.

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Supporting Information Available: X-ray crystal structure data for **2b**, ^{1}H NMR spectra for the products of the reaction between **1a** and 4-acetoxy-2-butanone, and a mechanistic scheme for transesterification and elimination reactions mediated by metal alkoxides. This material is available free of charge via the Internet at http://pubs.acs.org.

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