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Immortal ring-opening polymerization of β-butyrolactone with zinc catalysts: Catalytic approach to poly(3-hydroxyalkanoate)

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ABSTRACT

The zinc alkoxide complex prepared in situ from the reaction of (BDI)Zn(N(SiMe$_3$)$_2$) (BDI = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)imino)-2-pentene) with ROH (R = *i*Pr or Bn = CH_2Ph) is an efficient catalyst for both the solution and bulk ring-opening polymerization (ROP) of *racemic*-β-butyrolactone (BBL). The controlled "immortal" ROP of BBL using the binary catalytic system (BDI)Zn(N(SiMe$_3$)$_2$)/BnOH, where the alcohol acts both as co-initiator and chain transfer agent, proceeds smoothly under mild conditions (solution or bulk, 23–90 °C) to produce atactic poly(3-hydroxybutyrate) with moderate to high molar mass. For the first time, PHBs could be prepared from very small loadings of a metallic catalyst (100 ppm) via an "immortal" procedure, thereby allowing the growth of as many as 50–200 PHBs chains per metal center. Well-defined α-hydroxy,ω-alkoxy ester telechelic PHBs, of molar mass ranging up to $\overline{M}n = 42,600$ g mol^{-1} were thus quantitatively obtained and fully characterized by NMR, MALDI-TOF MS and SEC analyses.

1. Introduction

Poly(3-hydroxybutyrate) (PHB) produced by bacteria and other living organisms is known as the simplest and most common member of the naturally derived aliphatic polyesters that are the poly(hydroxyalkanoate)s (PHAs) [1]. Owing to its biocompatibility, biodegradability and to a broad range of mechanical properties, materials derived from PHB and its copolymers have emerged as promising candidates in a host of applications dealing within microelectronics and the biomedical field, especially in tissue or bone engineering and drug delivery applications (pins, plates, anti-cancer drug carrier…) [1,2].

To enlarge the volume of manufactured PHB as well as to overcome the high production cost of the fermentation synthetic route, several chemical synthetic approaches have been developed [1,3]. Besides ring-opening carbonylative polymerization of epoxides with discrete metal-based homogenous catalysts, for which important challenges such as the synthesis of high molar mass PHA still remain [4], the other main way to access to PHBs is the ring-opening polymerization (ROP) of β-butyrolactone (BBL). Unlike the bacteria-mediated route which only affords isotactic PHB, such controlled processes do enable the preparation of a wide variety of PHB microstructures. Atactic PHB, as well as PHB enriched to different extents in isotactic and syndiotactic diads have been prepared from racemic-BBL (*rac*-BBL). This leading technique revolves around metal (essentially aluminum, zinc, tin or rare-earths) containing complexes as initiating species for the ROP of BBL [5,6]. Most remarkable is the single site β-diiminate zinc alkoxide catalyst developed by Coates, (BDI)Zn(O*i*Pr) (BDI = CH(C-MeNC$_6$H$_3$-2,6-*i*Pr$_2$)$_2$), which enables the controlled living ROP of BBL giving high molar mass atactic PHBs ($\overline{M}n$ up to 144,000 g mol^{-1}; $\overline{M}w/\overline{M}n = 1.06 - 1.21$) with high reaction rates,[5] and with similar high efficiencies as observed for the living stereoselective ROP of lactide [7]. Later on, some rare-earth alkoxides derivatives have surpassed the performance of these β-diiminate zinc catalysts [8]. Some yttrium-alkoxide complexes supported by amino-alkoxy-bis(phenolate) ligands exhibited the highest activity and greatest stereoselectivity for the syndiospecific polymerization of *rac*-BBL [8c,d]. Fine tuning of the *ortho*-phenolate substituents on the tetradentate ligand allowed the preparation of PHB ($\overline{M}n$ up to 64,300 g mol^{-1}, $\overline{M}w/\overline{M}n = 1.03 - 1.18$) with a degree of syndiotacticity ranging from 80 to 96% [8c,d]. Bis(guanidinate) lanthanide alkoxide complexes have been shown to promote the stereoselective ROP of *racemic*-BBL to afford syndiotactic PHB through a chain-end controlled mechanism, while they remained surprisingly non-stereoselective for the ROP of *racemic*-lactide under similar experimental conditions [8e].

Within the current concern about the removal of possibly toxic metal remnants in the final polymers, and especially in the context

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of macromolecules designed for biomaterial functions or microelectronics, other ROP methods involving simple organic molecules as initiating species have appeared more recently [3a,9]. While these are mainly dealing with lactide, trimethylene carbonate, or larger lactones (ε-caprolactone, δ-valerolactone) [10], well-defined, quite high molar mass PHBs ($\overline{M}n$ up to 34,900 g mol^{-1}, $\overline{M}w/\overline{M}n = 1.1 - 1.3$) with end-group fidelity have been recently synthesized from the "controlled-living" ROP of BBL using carbenes based metal-free catalytic systems [11].

In between these two approaches lies the strategy based on "immortal" ROP (iROP) of a cyclic monomer. iROP, initially introduced by Inoue for the cationic ROP of epoxides using an aluminum-porphyrin/alcohol catalytic system, involves reversible transfer reactions in a "living" ROP process [12–14]. It relies on the use of a metallic complex, combined to a protic source (commonly an alcohol) that behaves simultaneously as a co-initiator and as a chain transfer agent (CTA). Since this pioneering work, it has been applied to the ROP of cyclic esters, typically ε-caprolactone and lactide [15]. We have also investigated this concept for the controlled ROP of lactides [16] and trimethylene carbonate [17], paying special efforts to minimize metal loadings and employ large amounts of CTA, to eventually optimize catalytic productivity and activity. We thus developed efficient procedures that involve very small metal complex loadings (as low as 20 ppm vs monomer) for the synthesis of well-defined polyesters of controlled molecular features (especially molar mass, molar mass distribution, end-group fidelity or microstructures) [16,17].

We have now investigated the "immortal" ROP of β-butyrolactone. This monomer is much more recalcitrant than the aforementioned ε-caprolactone, lactides, and trimethylene carbonate. As a matter of fact, only one example of iROP of BBL is known, using the (tetraphenylporphyrinato)-aluminum carboxylate complex combined to a protic compound such as hydrogen chloride or carboxylic acids [15b]; yet, the overall performances remained modest, with productivities limited to 800 equiv of BBL vs Al and formation of only PHB oligomers of molar mass ranging from $\overline{M}n = 950$ to 1800 g mol^{-1}. Also, although very effective for the living ROP of *rac*-BBL [8c] and also quite effective for the iROP of *rac*-lactide [16], yttrium complexes supported by alkoxy-amino-bis(phenolate)s ligands developed in our group never proved able to achieve iROP of *rac*-BBL; actually, when more than 5 equiv of alcohol (vs Y) are used, the catalytic activity drops dramatically for reasons that remain still unclear to date. We then evaluated the catalytic system composed of the increasingly ubiquitous β-diiminate amido precursor, (BDI)Zn(N(SiMe$_3$)$_2$), combined to an alcohol [5,7]. Indeed, the alkoxide derived from this complex upon reaction with 2-propanol allows the living and controlled synthesis of tailored PHBs [7]. Second, in situ formation of zinc alkoxide initiating species from either amide (e.g. Zn(N(SiMe$_3$)$_2$)$_2$) or alkyl (e.g. ZnEt$_2$) derivatives and various types of hydroxyl-containing reagents in the ROP of cyclic monomers is now a well spread approach avoiding the prior isolation of the active alkoxide complex. Indeed previous works have showed that the OR group(s) on the catalyst thus generated, directly initiate the polymerization at rates competitive with propagation hence allowing a good control of the polymerization [7c,d,17,18]. In this paper, we thus describe both the solution and bulk "immortal" ROP of BBL using the [(BDI)Zn(N(SiMe$_3$)$_2$)]/ROH catalytic systems.

2. Experimental part

2.1. Materials

All manipulations were performed under inert atmosphere (argon, <3 ppm of O_2) using standard Schlenk, vacuum line and glove-box techniques. Solvents were thoroughly dried and deoxygenated by standard methods and distilled before use. $CDCl_3$ was dried over a mixture of 3 and 4 Å molecular sieves. Benzyl alcohol (BnOH, Acros) was distilled under argon atmosphere and kept over activated 4 Å molecular sieves. β-butyrolactone (BBL, TCI Europe) was dried three times over CaH_2 before use. (BDI)Zn(N(SiMe$_3$)$_2$) and [(BDI)Zn(O*i*Pr)]$_2$ were synthesized following literature procedures [7b].

2.2. Instrumentation and measurements

^{1}H (500, 200 MHz) and ^{13}C (125, 50 MHz) NMR spectra were recorded in $CDCl_3$ on Bruker Avance AM 500 and DPX 200 spectrometers at 23 °C. Chemical shifts (δ) are reported in ppm and were referenced internally relative to tetramethylsilane ($\delta = 0$) using the residual ^{1}H and ^{13}C solvent resonance.

Average molar mass ($\overline{M}n$) and molar mass distribution ($\overline{M}w/\overline{M}n$) values were determined by SEC in THF at 20 °C (flow rate = 1.0 mL min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a PLgel 5 Å MIXED-C column. The polymer samples were dissolved in THF (2 mg mL^{-1}). All elution curves were calibrated with polystyrene (PS) standards ($\overline{M}n_{SEC}$ values are uncorrected for possible difference in hydrodynamic volume of PHB vs PS) [7b,8d]. The SEC traces of the polymers all exhibited a unimodal and symmetrical peak, unless otherwise specified.

The molar mass values of short-chain H-PHB-OBns ($Mn < 16000$ gmol^{-1}) were determined by ^{1}H NMR analysis, from the relative intensity of the signals of the methine protons of the PHB chains ($CH_2CH(CH_3)(O)$, $\delta = 5.25$ ppm) to the aromatic protons of the chain-end ($(CO)OCH_2C_6H_5$, $\delta = 7.34$ ppm). The number-average molar mass values thus obtained by ^{1}H NMR, $\overline{M}n_{NMR}$, were in close agreement with the ones calculated, as reported in Tables 1–4.

Monomer conversions were calculated from ^{1}H NMR spectra of the crude polymer sample, from the integration (Int.) ratio Int.PHB/[Int.PHB + Int.BBL], using the methine proton ($CH_2CH(CH_3)(O)$) of the polymer at $\delta = 5.25$ ppm and of the monomer at $\delta = 4.66$ ppm.

MALDI-TOF mass spectra were recorded with a AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N_2 laser source (337 nm, 4 ns pulse width) and time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and an accelerating voltage of 70 kV. The polymer sample was dissolved in $CHCl_3$ (10 mg mL^{-1}) and a THF solution of dithranol (10 mg mL^{-1}) was prepared. Both solutions were then mixed in a 5:2 volume ratio respectively and 1 μL of the final solution was deposited on the sample target and then air-dried.

2.3. Typical polymerization procedure

(BDI)Zn(N(SiMe$_3$)$_2$) (0.010 g, 15 μmol) was added to BnOH (1 equiv., 1.6 μL, 15 μmol) placed in toluene (0.1 mL) and stirred over 30 min just prior to the addition of the BBL monomer (133 mg, 1.5 mmol). The mixture was then stirred at the desired temperature over the appropriate time period (reaction times were not systematically optimized). The reaction was quenched with an excess of an acetic acid solution (ca. 2 mL of a 1.74 mol/L solution in toluene). The resulting mixture was concentrated under vacuum and the conversion determined by ^{1}H NMR analysis of the residue. The crude polymer was then dissolved in CH_2Cl_2 and purified upon precipitation in cold methanol, filtered and dried under vacuum. **H-PHB-OBn** = $HOCH(CH_3)CH_2CO(O)\{CH(CH_3)CH_2C(O)O\}_nCH_2C_6H_5$: ^{1}H NMR (500 MHz, $CDCl_3$,): δ 7.34 (s, 5H, $C_6H_5CH_2O$), 5.25 (m, nH, $CH_2CH(CH_3)OC(O)$), 5.11 (s, 2H, $C_6H_5CH_2O$), 4.20 (br s, 1H,

Table 1
Solution (immortal) ring-opening polymerization of *rac*-BBL initiated by [(BDI)Zn(O*i*Pr)]$_2$/*i*PrOH in toluene.

Entry	[Zn]$_0$ (mmol.L^{-1})	[BBL]$_0$/[Zn]$_0$/[*i*PrOH]$_0$[a]	Temp. (°C)	Reaction Time[b] (min)	Conv.[c] (%)	$\overline{M}n_{theo}$[d] (g mol^{-1})	$\overline{M}n_{NMR}$[c] (g mol^{-1})	$\overline{M}n_{SEC}$[e] (g mol^{-1})	$\overline{M}w/\overline{M}n$[f]
1	23.1[g]	100/1/0	23	35	90	7800	12,100	18,000	1.14
2	10.2	200/1/0	23	70	80	13,800	13,700	22,000	1.14
3	10.2	200/1/0	60	15	60	10,400	10,300	28,000	1.15
4	10.2	200/1/5	23	70	50	1800	1700	2000	1.15
5	4	500/1/0	60	60	78	33,600	–	27,300	1.20
6	4	500/1/2	60	60	70	15,100	13,190	10,800	1.20
7	4	500/1/5	60	60	51	4400	4400	4800	1.20

[a] Monomer and alcohol equivalents relative to [Zn]$_0$ = [(BDI)Zn(O*i*Pr)]$_0$ with [BBL]$_0$ = 2.0 mol L^{-1}.
[b] Reaction times were not necessarily optimized.
[c] Monomer conversion and average molar mass value determined by ^{1}H NMR.
[d] Calculated from [BBL]$_0$/[(BDI)Zn(O*i*Pr)]$_0$ × monomer conversion × M_{BBL} + M_{HoiPr}, or from [BBL]$_0$/([(BDI)Zn(O*i*Pr)]$_0$ + [HO*i*Pr]$_0$) × monomer conversion × M_{BBL} + M_{HoiPr} with M_{BBL} = 86 g mol^{-1} and M_{iPrOH} = 60 g mol^{-1}.
[e] Determined by SEC vs polystyrene standards (uncorrected values).
[f] Molar mass distribution calculated from SEC traces.
[g] Experiment performed in C_6D_6.

$CH_2CH(CH_3)OH$), 2.53 (m, 2n + 2H, $CH_2CH(CH_3)OC(O)$, $CH_2CH(CH_3)OH$), 1.27 (m, J = 6 Hz, 3n + 3H, $CH_2CH(CH_3)OC(O)$, $CH_2CH(CH_3)OH$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8 (s, $C_6H_5CH_2OC(O)$), 169.1 (m, $CH_2CH(CH_3)OC(O)$), 135.7 (s, $C_5H_5CCH_2OC(O)$), 128.4 (d, $C_5H_5CCH_2OC(O)$), 67.6 (m, $CH_2CH(CH_3)OC(O)$), 66.4 (s, $C_6H_5CH_2OC(O)$), 64.2 (d, $CH_2CH(CH_3)OH$), 43.2 (s, $CH_2CH(CH_3)OH$), 40.6 (d, $CH_2CH(CH_3)OC(O)$), 22.3 (s, $CH_2CH(CH_3)OH$), 19.7 (s, $CH_2CH(CH_3)OC(O)$). **H-PHB-OiPr** = $HOCH(CH_3)CH_2CO(O)\{CH(CH_3)CH_2C(O)O\}_nCH(CH_3)_2$: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.22 (quint, nH, $CH_2CH(CH_3)OC(O)$), 4.97 (m, 1H, $Me_2CHOC(O)$), 4.15 (br s, 1H, $CH_2CH(CH_3)OH$), 2.57, 2.44 (m, 2n + 2H, $CH_2CH(CH_3)OC(O)$, $CH_2CH(CH_3)OH$), 1.25 (m, J = 6 Hz, 3n + 3H, $CH_2CH(CH_3)OC(O)$, $CH_2CH(CH_3)OH$); 1.20 (m, 1H, $Me_2CHOC(O)$).

3. Results and discussion

The investigation of the iROP of *rac*-BBL was first carried out in solution from the isolated [(BDI)Zn(OiPr)]$_2$ as preliminary studies, followed by more extensive examinations (solution and bulk) using the composite system (BDI)Zn(N(SiMe$_3$)$_2$)/*i*PrOH or BnOH prepared in situ.

Selected results gathered in Table 1 confirmed that the solution ROP of *rac*-BBL using previously isolated [(BDI)Zn(O*i*Pr)]$_2$, produces atactic PHB (vide infra), as initially disclosed by Coates [5]. Temperature effects examined by comparing the polymerization rate at room temperature and at 60 °C at [BBL]$_0$/[[(BDI)Zn(O*i*Pr)]$_2$]$_0$ = 200 expectedly verified [5] the advantageous impact of a higher operating temperature, while maintaining the control (entries 2–3). We then evaluated, as preliminary investigations, the behavior of the [(BDI)Zn(O*i*Pr)]$_2$/*i*PrOH system in the solution iROP of BBL (entries 2, 4, 5–7). The lowering of the polymer molar mass in accordance with the increasing amounts of 2-propanol introduced as CTA in the reaction medium, revealed the potential of this alkoxide catalyst to undergo iROP of *rac*-BBL. Up to five macromolecules could be thus successfully grown from a unique zinc center, giving PHB of well controlled molar mass and molar mass distributions ($\overline{M}w/\overline{M}n < 1.17$). The molar mass values determined by NMR spectroscopy ($\overline{M}n_{NMR}$, refer to the Experimental section) were in good agreement with the calculated ones ($\overline{M}n_{theo}$ as determined from the initial concentration in CTA, *i.e.*, in [*i*PrOH]$_0$, rather than from that of the zinc complex, vide infra) based on the monomer-to-alcohol ratio.

Motivated by these preliminary results on the solution iROP of *rac*-BBL with a well-defined but rather complicated to prepare complex (as compared to its amido precursor), we next evaluated the possibility to form the active alkoxide zinc complex in situ from the [(BDI)Zn(N(SiMe$_3$)$_2$)]/HO*i*Pr system. Representative results are summarized in Table 2. A reference experiment performed in absence of any added alcohol, that is the ROP carried out with the amido derivative (BDI)Zn(N(SiMe$_3$)$_2$), showed no significant polymerization of *rac*-BBL at room temperature over more than one hour (entry 1). In contrast, under similar operating conditions, with (BDI)Zn(N(SiMe$_3$)$_2$) in the presence of one equiv. of iPrOH, the ROP

Table 2
Solution "immortal" ring-opening polymerization of *rac*-BBL initiated by [(BDI)Zn(N(SiMe$_3$)$_2$)]/*i*PrOH in toluene.

Entry	[Zn]$_0$ (mmol L^{-1})	[BBL]$_0$/[Zn]$_0$/[*i*PrOH]$_0$[a]	Temp. (°C)	Reaction Time[b] (min)	Conv.[c] (%)	$\overline{M}n_{theo}$[d] (g mol^{-1})	$\overline{M}n_{NMR}$[c] (g mol^{-1})	$\overline{M}n_{SEC}$[e] (g mol^{-1})	$\overline{M}w/\overline{M}n$[f]
1	10.3	200/1/0	23	70	<2	<400	–	–	–
2	20.6	100/1/1	23	50	37	3200	2100	2200	1.25
3	20.6	100/1/1	60	70	96	8300	6800	5100	1.13
4	20.6	100/1/2	60	70	100	4400	3500	3900	1.13
5	20.6	100/1/5	60	70	100	1800	2100	2400	1.08
6	20.6	100/1/10	60	80	100	900	1100	800	1.07
7	10.3	200/1/1	23	70	20	3500	2200	2400	1.18
8	10.3	200/1/1	60	70	65	11,200	9000	7100	1.20
9	20.6	200/1/1[g]	60	70	79	13,600	10,500	7200	1.33
10	10.3	200/1/2	60	140	91	7900	6700	10,200	1.09
11	10.3	200/1/5	60	140	99	3500	4100	5300	1.08
12	10.3	200/1/10	60	150	98	1700	1800	2000	1.09

[a] Monomer and alcohol equivalents relative to [Zn]$_0$ = [(BDI)Zn(N(SiMe$_3$)$_2$)]$_0$ with [BBL]$_0$ = 2.0 mol L^{-1}.
[b] Reaction times were not necessarily optimized.
[c] Monomer conversion and average molar mass value determined by ^{1}H NMR.
[d] Calculated from [BBL]$_0$/[*i*PrOH]$_0$ × monomer conversion × M_{BBL} + M_{iPrOH}, with M_{BBL} = 86 g mol^{-1} and M_{iPrOH} = 60 g mol^{-1}.
[e] Determined by SEC vs polystyrene standards (uncorrected value).
[f] Molar mass distribution calculated from SEC traces.
[g] [BBL]$_0$ = 4.0 mol L^{-1}.

Table 3
Solution "immortal" ring-opening polymerization of *rac*-BBL initiated by [(BDI)Zn(N(SiMe$_3$)$_2$)]/BnOH in toluene.

Entry	$[Zn]_0$ (mmol L^{-1})	$[BBL]_0/[Zn]_0/[BnOH]_0$[a]	Temp. (°C)	Reaction Time[b] (min)	Conv.[c] (%)	$\overline{M}n_{theo}$[d] (g mol^{-1})	$\overline{M}n_{NMR}$[c] (g mol^{-1})	$\overline{M}n_{SEC}$[e] (g mol^{-1})	$\overline{M}w/\overline{M}n$[f]
1	20.6	100/1/1	23	50	84	7300	5700	4700	1.20
2	10.3	200/1/1	23	70	70	12,100	9600	10,200	1.14
3	10.3	200/1/1	23	100	81	14,000	10,300	11,100	1.20
4	20.6	100/1/1	60	15	100	8700	8400	8,800	1.17
5	20.6	100/1/2	60	15	100	4300	3900	2800	1.22
6	20.6	100/1/5	60	18	100	1700	1500	1400	1.17
7	20.6	100/1/10	60	20	85	900	800	800	1.18
8	10.3	200/1/1	60	15	85	14,700	13,300	11,100	1.20
9	10.3	200/1/2	60	20	100	8700	8200	8100	1.15
10	10.3	200/1/5	60	20	98	3500	3600	4200	1.18
11	10.3	200/1/10	60	20	93	1700	1800	2000	1.09
12	4.1	500/1/1	60	60	86	37,100	–	23,400	1.20
13	4.1	500/1/2	60	60	80	17,300	15,700	19,800	1.19
14	4.1	500/1/5	60	60	73	6300	6700	8,300	1.14
15	4.1	500/1/10	60	60	45	2000	1800	1400	1.70
16	4.1	500/1/10	60	120	61	2700	1400	mm[g]	1.75
17	4.1	500/1/20	90	80	96	2200	2200	mm[g]	mm[g]
18	4.1	500/1/50	90	80	96	900	840	mm[g]	mm[g]

[a] Monomer and alcohol equivalents relative to $[Zn]_0 = [(BDI)Zn(N(SiMe_3)_2)]_0$ with $[BBL]_0 = 2.0$ mol L^{-1}.
[b] Reaction times were not necessarily optimized.
[c] Monomer conversion and average molar mass value determined by ^{1}H NMR.
[d] Calculated from $[BBL]_0/[BnOH]_0 \times$ monomer conversion $\times M_{BBL} + M_{BnOH}$, with $M_{BBL} = 86$ g mol^{-1} and $M_{BnOH} = 108$ g mol^{-1}.
[e] Determined by SEC vs polystyrene standards (uncorrected value).
[f] Molar mass distribution calculated from SEC traces.
[g] Multimodal molar mass distribution.

proceeded. The apparent reaction rates observed were, however, greater in the case of the preformed discrete catalyst. For instance, at $[BBL]_0/[(BDI)Zn(OiPr)]_0 = 200$, polymerization from isolated $[(BDI)Zn(OiPr)]_2$ reached 80% conversion in 70 min at 23 °C (Table 1, entry 2), whereas only 20% was achieved from the [(BDI)Zn(N(SiMe$_3$)$_2$)]/HO*i*Pr (1:1) one-pot system (Table 2, entry 7). Likewise, a similar amount of monomer (60–65%) was polymerized at 60 °C, yet over only 15 min with isolated $[(BDI)Zn(OiPr)]_2$ (Table 1, entry 3) compared to 70 min with the in situ [(BDI)Zn(N(SiMe$_3$)$_2$)]/HO*i*Pr system (Table 2, entry 8). These observations may suggest that only part of the amido precursor is effectively converted to active isopropoxide species under these conditions. Indeed, if

Table 4
Bulk "immortal" ring-opening polymerization of *rac*-BBL initiated by [(BDI)Zn(N(SiMe$_3$)$_2$)]/BnOH.

Entry	$[BBL]_0/[Zn]_0/[ROH]_0$[a]	Temp. (°C)	Reaction Time[b] (min)	Conv.[c] (%)	$\overline{M}n_{theo}$[d] (g mol^{-1})	$\overline{M}n_{NMR}$[c] (g mol^{-1})	$\overline{M}n_{SEC}$[e] (g mol^{-1})	$\overline{M}w/\overline{M}n$[f]
1	200/1/1	60	10	88	15,300	12,400	11,600	1.16
2	200/1/5	60	20	100	3500	3600	3200	1.27
3	200/1/10	60	20	99	1800	1700	2200	1.11
4	200/1/20	60	25	80	970	770	670	1.13
5	500/1/1	60	60	94	41,200	–	21,100	1.16
6	500/1/5	60	40	85	8700	8700	7900	1.06
7	500/1/10	60	60	73.5	3300	3000	4800	1.05
8	500/1/20	60	80	75	1700	1400	2200	1.10
9	500/1/50	60	120	84	830	830	700	1.13
10	800/1/1	60	90	77	53,100	–	35,000	1.22
11	800/1/2	60	100	76	26,200	–	18,700	1.07
12	800/1/5	60	120	74	10,300	8900	9500	1.08
13	800/1/10	60	200	84	5900	5100	7800	1.07
14	1000/1/1	60	360	76	65,600	–	42,600	1.26
15	1000/1/5	60	360	83	14,300	11,300	12,500	1.28
16	1000/1/10	60	420	71	6200	5100	5000	1.07
17	1000/1/20	60	420	77	3400	3900	4300	1.07
18	1000/1/50	60	420	79	1800	1200	1100	1.10
19	1000/1/50	60	1410	90	1700	1400	1400	1.09
20	1000/1/50	90	180	97	1800	1600	1500	1.12
21	2000/1/10	60	1440	74	12,900	11,900	12,600	1.09
22	2000/1/50	90	300	48	1700	1800	2000	1.09
23	2000/1/100	90	330	58	1100	800	740	1.11
24	2000/1/200	90	360	19	200	270	–	–
25	5000/1/10	90	900	33	14,300	19,600	24,600	1.07
26	5000/1/50	90	900	60	5200	5500	5700	1.04
27	10,000/1/10	90	4620	21	18,200	12,900	21,000	1.10

[a] Monomer and alcohol equivalents relative to $[Zn]_0 = [(BDI)Zn(N(SiMe_3)_2)]_0$.
[b] Reaction times were not necessarily optimized.
[c] Monomer conversion and average molar mass value determined by ^{1}H NMR.
[d] Calculated from $[BBL]_0/[BnOH]_0 \times$ monomer conversion $\times M_{BBL} + M_{BnOH}$, with $M_{BBL} = 86$ g mol^{-1} and $M_{BnOH} = 108$ g mol^{-1}.
[e] Determined by SEC vs polystyrene standards (uncorrected value).
[f] Molar mass distribution calculated from SEC traces.

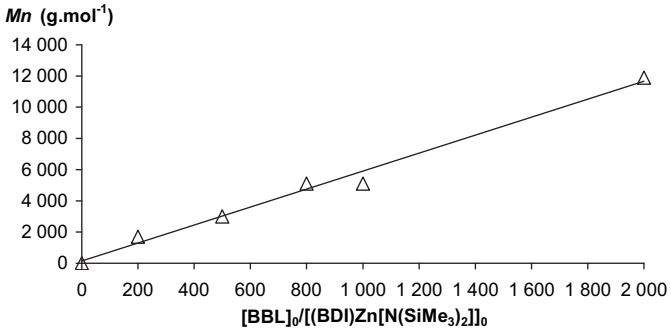


Fig. 1. Dependence of the experimental molar mass determined by NMR, $\overline{M}n_{NMR}$, on the $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0$ ratio for the bulk ROP of *rac*-BBL with $[(BDI)Zn(N(SiMe_3)_2)]_0/[BnOH]_0 = 1/10$ (Table 4).

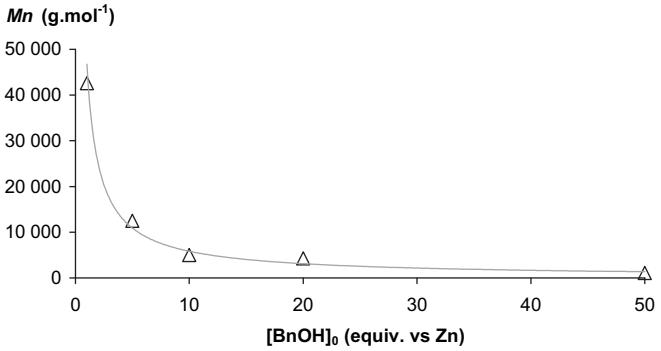


Fig. 2. Dependence of the experimental molar mass determined by SEC, $\overline{M}n_{SEC}$, of PHBs on the amount of added benzyl alcohol for the bulk iROP of *rac*-BBL initiated by the $(BDI)Zn(N(SiMe_3)_2)$/BnOH system at $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0 = 1000/1$ (Table 4).

the conversion of the amide to the isopropoxide species only partly occurs (what we assume, as this accounts for the decrease of the apparent ROP rate), the free isopropanol left in the reaction medium can then act as a chain transfer agent vs the propagating Zn-poly(hydrobutyrate) alkoxy species. Therefore, the Mn value of the polymer is then determined by the [BBL]/([(BDI)Zn(OR)] + free *i*PrOH) that is the $[BBL]_0/[i\text{PrOH}]_0$ (where $[ROH]_0$ is the initial concentration of *i*PrOH added in the experiment) rather than by the $[BBL]_0/[(BDI)Zn(OR)]_0$ ratio. A good match between the experimental and theoretical molar mass values is still therefore expected, even though less active Zn-species is formed in the reaction medium. Note, however, that these reactions with the *in situ* system proceeded with a similar control of molar masses as that obtained from the isolated zinc alkoxide derivative $[(BDI)Zn(O\text{i}Pr)]_2$[†].

Investigation of the solution iROP of BBL from this $[(BDI)Zn(N(SiMe_3)_2)]$/HO*i*Pr catalytic system at 60 °C showed the decrease of the polymer molar mass proportionally to the amount of added alcohol (Table 2, entries 3–6, 8,10–12). This observation thereby highlights the successful withstanding of the alkoxide prepared in situ toward increasing incoming amounts of HOiPr, leading to successful reversible transfer between dormant and active species (vide infra).[*] This further revealed that the alkoxide $[(BDI)Zn(OiPr)]_2$ prepared in situ from the amide precursor ($(BDI)Zn(N(SiMe_3)_2)$) and 2-propanol successfully allows the controlled iROP of BBL affording well-defined PHBs.

The ROP of trimethylene carbonate initiated by this same $[(BDI)Zn(N(SiMe_3)_2)]$/ROH catalytic systems with ROH = *i*PrOH or BnOH having underlined the better ability of the benzyl alcohol to undergo controlled "immortal" ring-opening polymerization, especially in bulk [17], we next focused on the solution iROP of *rac*-BBL with this system (Table 3) and then compared it to the bulk process (Table 4).

Initial experiments for the ROP of *rac*-BBL ran in toluene solution at 23 °C using the $[(BDI)Zn(N(SiMe_3)_2)]$/BnOH (1:1) system confirmed that greater rates of polymerization are obtained when using benzyl alcohol instead of 2-propanol as co-initiator (Table 3). Higher apparent activities ($TOF = mol_{monomer}\, mol^{-1}_{initiator}\, h^{-1}$) were indeed reached with the heavier alcohol ($TOF = 100–120\ h^{-1}$, Table 3 entries 1, 2, vs $TOF = 34–44\ h^{-1}$, Table 2 entries 2, 7). As anticipated, raising the operating temperature from 23 °C to 60 °C also resulted in a substantial increase of the polymerization rate (Table 3, entries 1–3 vs 4, 8). In particular, quantitative conversion could be reached more rapidly at 60 °C, using BnOH in place of iPrOH, for the ROP in absence of transfer agent (i.e., in the presence of the only one equiv of BnOH/*i*PrOH required to form the alkoxide initiating species). At $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0 = 100$, with BnOH, the whole *rac*-BBL was converted into PHB at 60 °C within 15 min (Table 3, entry 4), whereas more than 70 min were required with *i*PrOH (Table 2, entry 3). Similarly, at the higher monomer loading of 200, as much as 170 equiv of BBL vs $(BDI)Zn(N(SiMe_3)_2)$ were polymerized within 15 min with BnOH while only 130 equiv of BBL were consumed in 70 min with *i*PrOH (Table 3, entry 8 vs Table 2, entry 8). Solution iROP of BBL could be achieved with up to 500 equiv of *rac*-BBL in presence of as many as 50 equiv. of BnOH (Table 3, entries 12–18), with almost quantitative conversion (96%) being reached upon raising the temperature to 90 °C (Table 3, entries 17–18). However, the molar mass distribution then became multimodal and the experiments lacked reproducibility (Table 3,

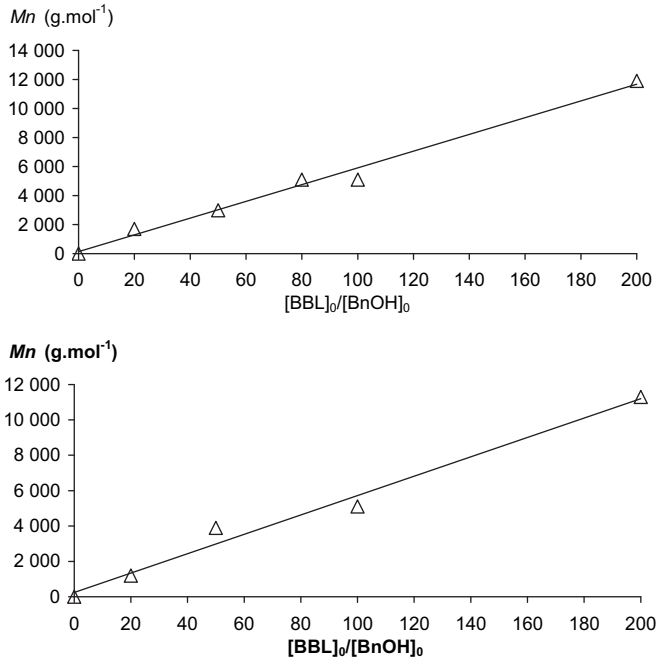


Fig. 3. Dependence of the experimental molar mass determined by NMR, $\overline{M}n_{NMR}$, of PHBs on the $[BBL]_0/[BnOH]_0$ ratio for the iROP of *rac*-BBL initiated by the $(BDI)Zn(N(SiMe_3)_2)$/BnOH system for $[(BDI)Zn(N(SiMe_3)_2)]_0/[BnOH]_0 = 1/10$ (top) and $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0 = 1000/1$ (bottom) (Table 4).

[†] The degree of polymerization is given by $DP_t = ([BBL]_0 - [BBL]_t)/([(BDI)Zn(O\text{i}Pr)]_t + [i\text{PrOH}]_t)$, with $[(BDI)Zn(O\text{i}Pr)]_t + [i\text{PrOH}]_t = [i\text{PrOH}]_0$.

[*] As previously evidenced, the discrete [(BDI)Zn] moiety remains stable towards large excess of alcohol [17c]. In fact, ^{1}H NMR monitoring of the reaction between $[(BDI)Zn(N(SiMe_3)_2)]$ and excess BnOH (10 equiv. vs. Zn) showed the stability over 24 h of the complex and especially of the BDI ligand that remains bound to the metal center (i.e., only $HN(SiMe_3)_2$ and not [BDI]H was released), along with the formation of the β-diiminate zinc-OBn bond.

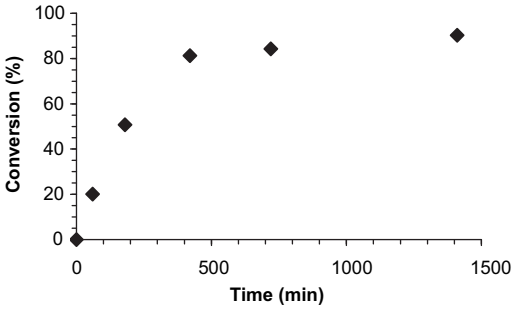


Fig. 4. Time dependence of the *rac*-BBL conversion at $[BBL]_0/[Zn]_0/[BnOH]_0 = 1000/1/50$ (refer to the Supporting Information).

entries 15–18). Once again, the PHB molar mass displayed a linear decrease with increasing amount of added BnOH CTA for each of the monomer-to-active-species ratio of 100, 200 or 500.

Aiming at achieving a "greener" operating procedure, and possibly moving further up the limits of the iROP of *rac*-BBL, we next investigated the solvent-free iROP using the (BDI)Zn(N(SiMe$_3$)$_2$)/BnOH catalyst system (Table 4). The $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0$ ratio was successfully increased stepwise from 200 up to 10,000 while the alcohol content was raised up to 200 equiv. vs the zinc complex.

At $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0/[BnOH]_0$ ratios of 200-1000/1/1, i.e. in "classical" bulk ROP conditions, the PHB molar mass values as determined by SEC ($\overline{M}n_{SEC}$) increased with BBL loadings (Table 4). The molar mass of the desired H-PHB-OBn could thus be monitored on demand upon tuning the $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0$ ratio. PHBs of molar mass ranging as high as $\overline{M}n_{SEC}$ = 42600 g mol^{-1}could thus be prepared (Table 4, entry 14). The quite narrow molar mass distribution values obtained in such bulk experiments ($\overline{M}w/\overline{M}n$ average value = 1.12), compared to the solution ROPs ($\overline{M}w/\overline{M}n$ average value = 1.24, Table 3), are unusual and reversed to what is more commonly observed [17]. These values apparently reflect that side-processes (transfer reactions and/or inter- and intra-molecular transesterifications, i.e. reshuffling and backbiting, respectively) all along the propagation step, are less important in bulk operating conditions [19]. Some side-

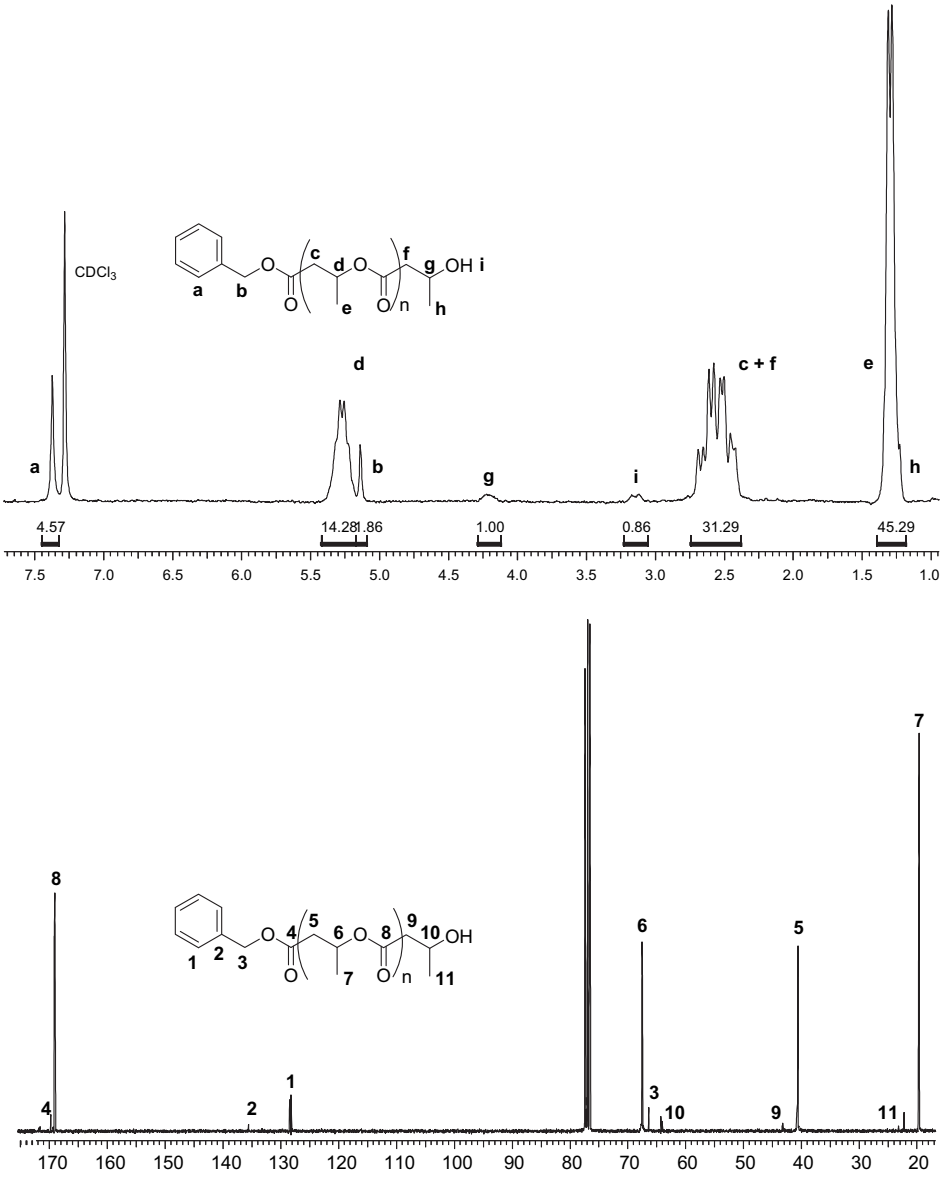
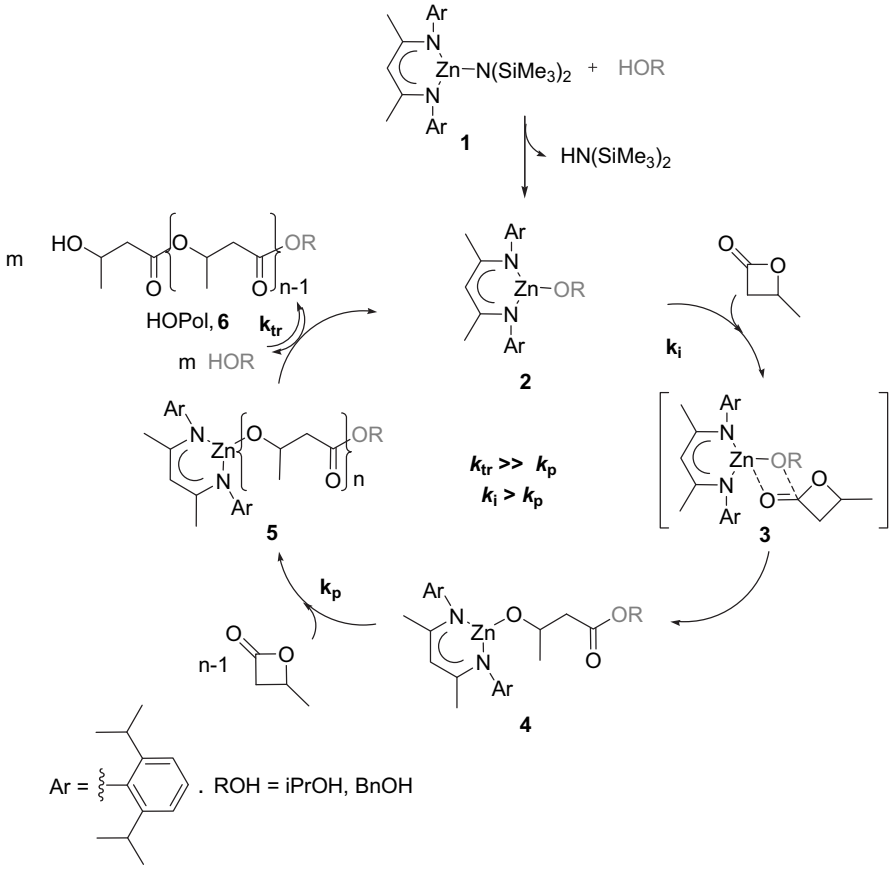


Fig. 5. ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C, top) and $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 23 °C, bottom) spectra of H-PHB-OBn ($\overline{M}n$ = 1400 g.mol^{-1}, Table 4, entry 19).

reactions, indeed typical of cyclic ester ROP and responsible for an increase of the observed $\overline{M}w/\overline{M}n$ values [19], do appear essentially at higher monomer loadings (800, 1000 equiv.; Table 4, entries 10, 14, 15). These quite narrow $\overline{M}w/\overline{M}n$ values thereby highlight the relatively good control of the ROP in both bulk and solution media.

Valuable information can be drawn from the bulk iROP of BBL experiments (Table 4). For a given CTA content (5, 10, 20, 50, 100 or 200 equiv. vs [(BDI)Zn(N(SiMe$_3$)$_2$)]), the polymerization remained quite well controlled in terms of the agreement of the experimental molar mass values determined by NMR ($\overline{M}n_{NMR}$) and monomer-to-alcohol ratios. A good molar mass control is demonstrated by the linear increase in $\overline{M}n_{NMR}$ with the monomer-to-zinc ratio at $[(BDI)Zn(N(SiMe_3)_2)]_0/[BnOH]_0 = 1/10$ (Fig. 1). Whichever the initial BBL loading (100–5000 equiv.), the decrease of the experimental molar mass $\overline{M}n_{NMR}$ and $\overline{M}n_{SEC}$ with the increase of the benzyl alcohol content, as depicted Fig. 2 at $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0 = 1000/1$, shows that the transfer occurs efficiently, thereby generating as many polymer chains as the number of added alcohol equivalents. The dependence of the experimental molar masses $\overline{M}n_{NMR}$ of PHBs on the monomer-to-alcohol ratio for 10 equiv of BnOH vs (BDI)Zn(N(SiMe$_3$)$_2$) and for a BBL-to-(BDI)Zn(N(SiMe$_3$)$_2$) ratio of 1000, is presented Fig. 3. As stated above, the occurrence of side-reactions is also observed at higher BBL loadings (800, 1000 equiv.) as evidenced by the small deviation between theoretical and experimental values (Fig. 3-top). Similarly, for $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0 = 1000$, the $\overline{M}n_{NMR}$ values display a linear relationship with the $[BBL]_0/[BnOH]_0$ ratio (Fig. 3-bottom). These observations illustrate the "controlled-living" character of the iROP reaction under a broad range of experimental conditions. Indirectly, this also hints that the active Zn(II) species is able to withstand quite large amounts of alcohol, as well as larger quantity of CTA in such bulk process, as compared to solution conditions. This quite good stability is most likely provided by the ancillary BDI ligand [5,7b,17]. Finally, the variation of the monomer conversion with time remained linear within the first 180–200 min, reaching a plateau afterwards with the conversion attaining 90% in 23 min (Fig. 4, refer to the Supporting information). Under our experimental reaction conditions, successful iROP of 1000 equiv. (1.33 g) of BBL with the simultaneous growth of up to 50 polymer chains per zinc center, could be reasonably achieved at 60 °C (entry 20). Upon doubling the monomer content to 2000 equiv, the iROP remained successful up to 90 °C with as much as 50 (entry 22) and even 100 BnOH equiv. (entry 23). The iROP limit could be displaced further to a $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0/[BnOH]_0$ ratio of 2000/1/200, 5000/1/50 and 10,000/1/10 (entries 24, 26, 27). However, reproducibility issues were sometimes met in the latter, very demanding conditions, which probably arose from deactivation of the active species by residual impurities in the monomer. The linear dependence of the PHB molar mass on the concentration of added alcohol as CTA we evidence in the present work clearly demonstrates the ability of the (BDI)Zn(N(SiMe$_3$)$_2$)/BnOH catalytic system to undergo iROP of BBL. This system affords, for the first time, in controlled "immortal" conditions, PHBs of high molar mass at least up to 24 600 g mol^{-1} in the case of $[BBL]_0/[(BDI)Zn(N(SiMe_3)_2)]_0/[BnOH]_0$ of 5000/1/10 (Table 4, entry 25).

The general strategy of this approach is outlined in Scheme 1. Initially, the in situ reaction of the amido precursor **1** with the first added alcohol molecule ROH results in the formation of the alkoxide complex **2** which is the real initiating species. Added BBL then undergoes coordination–insertion into the resulting zinc-alkoxide



Scheme 1. Mechanistic representation of the [(BDI)Zn(N(SiMe$_3$)$_2$)]/alcohol]-mediated "immortal" ring-opening polymerization of *rac*-BBL for the synthesis of α-hydroxy, ω-alkoxy ester telechelic PHBs.

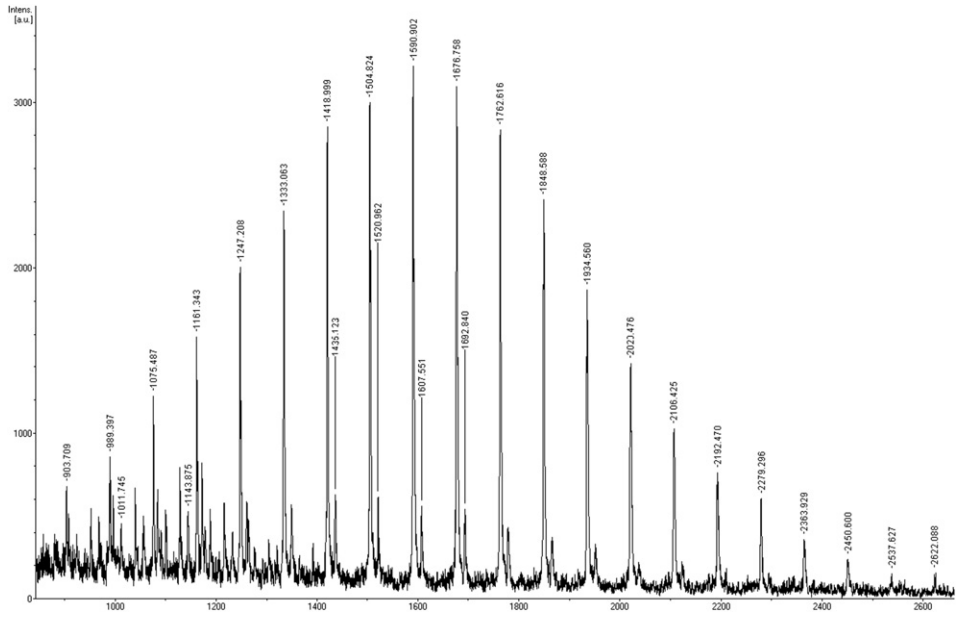


Fig. 6. MALDI-TOF mass spectrum of a H-PHB-OBn ($\overline{M}n$ = 1600 g mol^{-1}, Table 4, entry 20).

bond with oxygen–acyl bond cleavage of the monomer thus leading, via intermediate **3**, to **4**. Propagation proceeds with the growth of the polymer chain on the zinc center as an active species **5**. Concomitant chain transfer of living macromolecular species with (macro)molecules of alcohol gives rise to the H-PHBs-OR polymers.

As previously described in details [17], the key factor for a successful iROP relies on the chain transfer efficiency. This transfer reaction must be reversible and its rate must be greater than the rate of the propagation step ($k_{tr} >> k_p$), itself much lower than that of the initiation ($k_i > k_p$). As stated above, the molar mass distribution values $\overline{M}w/\overline{M}n$ values observed in the present study remain around 1.18 and always below 1.28 (Table 3 and 4), quite narrow values considering the bulk feature of the ROP process [19]. This observation supports that all CTA molecules do exchange with the active species faster than the polymer chains do grow. One can further outline that the process thus becomes catalytic vs the monomer and the macromolecules, as well as opposed to "classical-living" polymerizations where the number of macromolecules is given by the number of active sites available from the initiator molecules. In the present study, as many as 50–200 PHB chains could be successfully grown from a unique zinc center.

NMR analyses of the PHBs synthesized from all zinc systems first allowed confirming the regular chemical structure awaited for an oxygen–acyl bond cleavage of BBL. First, it must be noted that *trans*-crotonate and carboxy groups, which are often observed in the case of an anionic mechanism and also with the [Zn(BDI)(O*i*Pr)]$_2$ initiator in toluene solution at 75 °C [5], were not observed in the ^{1}H NMR spectra of these PHBs, noteworthy those prepared in bulk conditions even up to 90 °C. In addition, the exact nature of the polymer end-groups could be clearly identified as α-hydroxyl and ω-alkoxy ester groups. Examination of the precipitated polymer samples revealed, besides the main polymer chain signals, the typical resonances of a methylene group in α of an hydroxyl (δ = 4.20, br s, $CH_2CH(CH_3)OH$) and of the benzyl (δ = 7.34, s, $C_6H_5CH_2O$; 5.11, s, 2H, $C_6H_5CH_2O$) or isopropyl (δ = 4.97, m, $C(O)OCHMe_2$; 1.20, br s, $C(O)OCHMe_2$) ester function as illustrated in Fig. 5 with the ^{1}H and ^{13}C NMR spectra of H-PHB-OBn ($\overline{M}n_{NMR}$ = 1/41400 g mol^{-1}, Table 4, entry 19). This confirms the monomer opening at the O–acyl bond rather than via rupture of the O–alkyl one, which would have induced the formation of both a $-CH_2-C(O)OH$ and CH_2-CH_3 end-group, which signals are not observed [15b]. Finally, for short-chain PHBs, the molar mass values as determined by ^{1}H NMR analysis were in close agreement with the ones calculated $\overline{M}n_{theo}$ (refer to the Experimental section and Tables 1–4). Close examination of the carbonyl region of the ^{13}C NMR spectra confirmed the atactic microstructure of the PHBs prepared [8d].

MALDI-TOF-MS analysis of a low molar mass PHB ($\overline{M}n_{theo}$ = 1600 g mol^{-1}, Table 4, entry 20) clearly revealed a major population of PHBs unequivocally confirmed as $Na^+.H\{OC(Me)CH_2C(O)\}_nOBn$ (Fig. 6). The degree of polymerisation indicated by this spectrum (n = 17, $\overline{M}n_{MS}$ = 1590 g mol^{-1}) is in good agreement with the experimental value ($\overline{M}n_{NMR}$ = 1600 g mol^{-1}). The minor envelop observed ($\overline{M}n_{MS}$ = 1607 g mol^{-1}) corresponds to the K-cationized polymer distribution. The absence of $-N(SiMe_3)_2$ end-functionalized PHB population showed the absence of (BDI)Zn(N(SiMe$_3$)$_2$)-initiated polymerization, in agreement with the abovementioned inactivity of this complex at room temperature and further confirming its conversion into the initiating alkoxide complex (BDI)Zn(OBn).

4. Conclusion

It was previously reported that β-diiminate zinc alkoxides are extremely active catalysts for the solution ROP of BBL [5,7]. In this paper, we first demonstrate that active alkoxide zinc species can be suitably prepared just prior to the polymerization, thereby avoiding its previous limiting isolation. Furthermore, we have performed for the first time both the solution and bulk ROP of BBL from such an in situ zinc amide/alcohol catalytic system. The bulk ROP of BBL was originally performed in the present work and shown to successfully allow the well controlled synthesis of quite high molar mass PHBs under mild operating conditions. As much as 1000 equiv of BBL were effectively polymerized. Most significant, the "immortal" ROP of BBL was fruitfully carried out, both in solution and in bulk procedures, thereby affording the first example of an "immortal" living and controlled ROP of a β-lactone. PHBs could be prepared from minor loadings of a metallic catalyst (100 ppm), allowing the growth of as many as 50–200 PHBs chains per metal center. Significant advantages over previous procedures, besides a truly

low metal loading, include a lower reaction time as well as a solvent-free process. It must be highlighted that the key factor of the viability of such an iROP of BBL is most likely the β-diiminate-Zn complex. In this complex, the BDI ancillary provides great stability to the zinc center in presence of excess alcohol, preventing its decomposition [17b].

Acknowledgements

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.10.014.

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