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Stereoselective Ring-Opening Polymerization of Functional β -Lactones: Influence of the Exocyclic Side-Group †

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‡ These authors performed all the experimental work (except the mass spectrometry (P.J.) and chiral HPLC (M.B.) analyses) and contributed to the writing of the paper.

Abstract

Polyhydroxyalkanoates (PHAs) are a unique class of polyesters especially due to their chemical diversity imparted by their side-chain substituent that provides a handle to tune their properties, such as their thermal, mechanical and (bio)degradability signature. Here, we report that some functional PHAs, namely PBPL^{FG}s (FG = functional group), were synthesized by the controlled stereoselective ring-opening polymerization (ROP) of *racemic* 4-substituted- β -propiolactones, namely *rac*-BPL^{CH₂ZPh}s with Z = O, S, CH₂OCH₂, catalyzed by diamino- or amino-alkoxy-bis(phenolate) yttrium amido complexes (**1a–1g**) in the presence of isopropanol. Unprecedented syndio-enriched (*P_r* up to 0.87) PBPL^{CH₂ZPh}s of high molar mass (*M_{n,NMR}* up to 86,400 g mol^{−1}, *D_M* < 1.23) were thus typically prepared under mild operating conditions (toluene, 20 °C). Catalyst systems with smaller “uncrowded” Me or Cl *ortho*-substituents installed on the yttrium phenolate ligands (**1a–1c**) typically revealed less active than those with larger bulkier *t*Bu or CMe₂Ph groups (**1d–1g**), regardless of the monomer (TOF_{**1a–1c**} = 0.48–15 h^{−1}, TOF_{**1d–1g**} = 450–1840 h^{−1}). Irrespective of the catalyst system, exchanging oxygen with sulphur in BPL^{CH₂ZPh}s, with Z = O, S, did not affect the stereochemistry, always affording syndiotactic PBPL^{CH₂ZPh}s. On the other hand, either atactic or syndiotactic PBPL^{CH₂CH₂OCH₂Ph}s were formed upon tuning the catalyst from **1a–1c** or **1d–1g**, respectively. The intimate relationship, through “non-covalent” interactions, between the chemical nature of the exocyclic functional side-group on the β -lactone and the stereoelectronic tuning arising from the phenolate ligand *ortho*-substituents within the yttrium coordination sphere, modulated the stereocontrol of the ROP. The thermal behavior of these original functional PHAs depended closely on their side-chain substituent (*T_d^{onset}* = 226 to 272 °C; *T_g* = −15 to +40 °C).

Keywords: cyclic ester, functional β -propiolactone, β -lactone, non-covalent interactions, polyester, poly(hydroxyalkanoate) (PHA), ring-opening polymerization (ROP), stereoselective catalysis, yttrium

Graphical abstract

Introduction

Poly(β -hydroxyalkanoate)s (PHAs) are an important family of diversified natural and synthetic aliphatic polyesters renowned for their biodegradation in various environments. While natural PHAs are derived from biorenewable resources and produced by bacteria, synthetic PHAs are formed by ring-opening polymerization (ROP) of β -lactones. PHAs also differ one from another by the side-chain at the β -position of the repeating units along the backbone. Introduction of a pendant functional group (FG) along the polyester chains enables to access to chemically reactive PHAs and to polymers with different and tunable physico-chemical properties, thereby widening their range of applications.^{1,2} Within a worldwide increasing market, PHA materials can partially substitute any of the traditional fossil-based polymer families, especially polypropylene (PP) and polyethylene (PE); thus, their uses range from injection molding, extrusion, thermoforming, 3D printing, to foams, non-wovens, fibers, coatings, glues, adhesives, and paints. Besides, owing to their biocompatibility and biodegradability, PHAs are also being used in pharmaceutical, biomedical, cosmetic and packaging applications.³ PHAs are thus of topical interest especially as versatile green alternatives to single-use plastics with minimal environmental impact.⁴

Natural PHAs are isotactic crystalline polymers, as exemplified with poly(3-hydroxybutyrate) (PHB), the most ubiquitous PHA with a methyl group on the β -carbon, that displays a melting temperature (T_m) of 170–180 °C and a relatively low degradation temperature (ca. 256 °C), thus making difficult its processability and thereby somewhat limiting its commercial applications.⁵ Several features have been reported to influence the thermal properties of PHAs. Besides the nature of the side-chain, tacticity is one of the most critical determinants. Isotactic or syndiotactic stereoregular polymers are typically crystalline materials that display improved thermal and mechanical properties relative to their atactic counterparts. Therefore, developing synthetic strategies toward stereoregular PHAs is of great interest.

In this regard, the stereoselective ROP of chiral cyclic esters is a highly topical research field. A challenging objective is the synthesis of functional PHAs with a microstructure different from the naturally occurring isotactic PHAs, namely the

preparation of syndiotactic PHAs from readily available *racemic* β -lactone monomer(s). Extensive research over the past decades has demonstrated that rare-earth complexes combined with tetradentate bis(phenolate) ligands are highly efficient catalysts/initiators for the controlled ROP of chiral cyclic esters/carbonates, thereby affording synthetic polyesters/polycarbonates with different tacticities.^{6,7,8,9,10,11,12} In particular, achiral yttrium complexes with tripodal dianionic diamino- or aminoalkoxy-bis(phenolate) ligands $\{\text{ONXO}\}^{2-}$ ($\text{X} = \text{NMe}_2, \text{OMe}$) are, in the presence of an initiator (typically exogenous isopropanol), regarded as a “privileged” class of catalysts, due to their ability to promote the controlled ROP of heterocyclic monomers, their very high activity, and especially in light of their high stereoselectivity in the ROP of chiral cyclic esters such as of the ubiquitous *racemic* lactide,¹² or of *racemic trans*-cyclohexyl-ring-fused γ -butyrolactone (*rac*-GBL),¹³ *racemic trans*-cyclohexene carbonate,¹⁴ and of particular interest to our present research, the more reluctant-to-polymerize four membered-ring *racemic* β -lactones (BPL^{FG})^{12,15,16} (Scheme 1). It was thus previously demonstrated that yttrium complexes incorporating bulky aryl-containing substituents at the *ortho* positions of the phenolate ligands enable to access highly syndio-enriched PBPL^{Me} (i.e. PHB) from *racemic* β -butyrolactone (*rac*- BPL^{Me}) with a probability for syndiotactic enchainment (P_r = probability of racemic linkage; P_r = 1 for a perfectly syndiotactic polymer, P_r = 0 for an isotactic one, and P_r = 0.5 for an atactic one) up to 0.94.^{12c} These yttrium complexes also successfully promote the stereoselective ROP of higher functional cyclic esters such as the alkyl β -malolactonates (4-alkoxycarbonyl- β -lactones, $\text{BPL}^{\text{CO}_2\text{R}}$ with $\text{R} = \text{allyl}$ ($\text{All} = \text{CH}_2\text{CH}=\text{CH}_2$), benzyl ($\text{Bn} = \text{CH}_2\text{Ph}$)).¹⁵ Only the yttrium catalyst bearing small chloro, fluoro or methyl substituents installed at the *ortho* positions on the phenolate rings afford highly syndiotactic $\text{PBPL}^{\text{CO}_2\text{R}}$ ($P_r > 0.98$), while the incorporation of sterically crowded alkyl/aryl substituents (typically $\text{CMe}_2t\text{-Bu}$, $\text{CMe}_2\text{Ph} = \text{cumyl}$, CPh_3) on the aromatic rings provide significantly less syndio-enriched $\text{PBPL}^{\text{CO}_2\text{R}}$ ($P_r = 0.68\text{--}0.87$). Subsequently, the first highly stereoselective ROP of 4-alkoxymethylene- β -propiolactones (*rac*- $\text{BPL}^{\text{CH}_2\text{OR}_s}$, $\text{R} = \text{Me, All, Bn}$) by such yttrium complexes giving $\text{PBPL}^{\text{CH}_2\text{OR}_s}$ was reported.¹⁶ It was evidenced that a simple modification of the *R ortho*-

substituents on the $\{\text{ONXO}^{\text{R}_2}\}^{2-}$ platform of the yttrium catalyst from dicumyl to dichloro, induced a complete switch from a syndiospecific (P_r up to 0.91) to an isospecific (P_m up to 0.93) polymerization of $\text{rac-BPL}^{\text{CH}_2\text{OR}}_s$, respectively. DFT computations, focused on the first steps of these ROPs, attributed the origin of the isospecificity to strong C–H $\cdots$ Cl “second-sphere” or “non-covalent” interactions (NCIs) between the methylene hydrogens in the ring-opened monomer of the growing chain ($-\text{CHCH}_2(\text{OCH}_2\text{CH}=\text{CH}_2)$) and the *chloro* substituents of the ligand. Such NCIs arise from the attractive interactions induced by the halogen *ortho*-substituents on the phenolate ligand onto the methylene hydrogens of the last inserted monomer unit within the growing polymer chain.

Scheme 1. Stereoselective ROP of various chiral *racemic* 4-substituted- β -propiolactones $\text{rac-BPL}^{\text{FG}}_s$ (FG = Me, CO_2R , CH_2OR ; R = Me, All, Bn) catalyzed by diamino- or amino-alkoxy-bis(phenolate) yttrium isopropoxide $\text{Y}\{\text{ON}(\text{X})\text{O}^{\text{R}^1, \text{R}^2}\}/i\text{PrOH}$, affording the corresponding $\text{PBPL}^{\text{FG}}_s$, reported in the literature.^{8,12,15,16}

In this contribution, we first report the synthesis of the unprecedented functional $\text{PBPL}^{\text{CH}_2\text{ZPh}}_s$ by the ROP of the corresponding newly synthesized *racemic* β -propiolactones $\text{BPL}^{\text{CH}_2\text{ZPh}}_s$ (except of $\text{BPL}^{\text{CH}_2\text{OPh}}_s$, *vide infra*)¹⁷, promoted by diamino-

or amino-alkoxy-bis(phenolate) yttrium catalysts (**1a–1g**) in the presence of *i*PrOH as co-initiator (Scheme 2). These novel PHAs have then been thoroughly characterized by NMR spectroscopy, mass spectrometry, SEC, TGA and DSC analyses. Focus is next placed on the evaluation of the activity and the stereoselectivity of the catalyst systems, in relation to the chemical nature of the exocyclic pendant chain of the β -lactone combined to the stereoelectronic effects imparted by the yttrium ancillary ligand. The effect of the “O” vs “S” heteroatom on the polymerization of the substituted- β -propiolactones $\text{BPL}^{\text{CH}_2\text{ZPh}}_{\text{S}}$ ($\text{Z} = \text{O}, \text{S}$) is assessed. Comparison of the reactivity of *rac*- $\text{BPL}^{\text{FG}}_{\text{S}}$, where $\text{FG} = \text{CH}_2\text{OPh}$ vs $\text{CH}_2\text{OR}^{16}$ and COOR^{15} with $\text{R} = \text{Me}, \text{All}, \text{Bn}$, is also reported. Finally, insights into the contribution to the stereoselectivity control of exocyclic methylene hydrogens apart from the central oxygen within the side-arm of 4-alkoxyalkylidene- β -propiolactones, namely *rac*- $\text{BPL}^{\text{FG}}_{\text{S}}$ where $\text{FG} = \text{CH}_2\text{OPh}$ or $\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}$ vs $\text{CH}_2\text{OCH}_2\text{Ph}^{16}$, is probed.

Scheme 2. Stereoselective ROP of chiral 4-substituted- β -propiolactones *rac*- $\text{BPL}^{\text{CH}_2\text{ZPh}}_{\text{S}}$ ($\text{Z} = \text{O}, \text{S}, \text{CH}_2\text{OCH}_2$) catalyzed by diamino- or amino-alkoxy-bis(phenolate) yttrium complexes $\text{Y}\{\text{ONXOR}_2\}$ **1a–1g** in the presence of *i*PrOH, investigated in the present work.

Experimental section

Methods and materials

All manipulations involving organometallic catalysts were performed under inert atmosphere (argon, < 3 ppm O₂) using standard Schlenk, vacuum line, and glovebox techniques. Solvents were freshly distilled from Na/benzophenone under argon and degassed thoroughly by freeze-thaw-vacuum cycles prior to use. Isopropyl alcohol (Acros) was distilled over Mg turnings under argon atmosphere and kept over activated 3–4 Å molecular sieves. Bisphenol {ONXO^{R2}}H₂ prolignands and yttrium amide precursors of **1a–1g** were synthesized according to the methods reported in the literature.^{12b, 18} *Racemic* glycidyl phenyl ether (*rac*-G^{CH₂O^{Ph}}) was dried onto and distilled from CaH₂ and then stored over 3–4 Å activated molecular sieves (Sigma). *Racemic* 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂S^{Ph}})¹⁹ and 2-(2-(benzyloxy)ethyl)oxirane (*rac*-G^{CH₂CH₂OCH₂Ph})²⁰ were synthesized according to the literature, dried onto and distilled from CaH₂ and then stored over 3–4 Å activated molecular sieves (Figures S1–S5). Enantiopure (*S*)-phenyl glycidyl ether ((*S*)-G^{CH₂O^{Ph}}), (*S*)-2-((phenylthio)methyl)oxirane ((*S*)-G^{CH₂S^{Ph}}) and (*R*)-2-(2-(benzyloxy)ethyl)oxirane ((*R*)-G^{CH₂CH₂OCH₂Ph}) were prepared by hydrolytic kinetic resolution (HKR) of the corresponding *racemic* compound following the reported procedure (Figures S1–S5).²¹ *Rac*-BPL^{CH₂O^{Ph}}¹⁷ and [Salph(Cr(THF)₂)] [Co(CO)₄]²² were synthesized according to the literature procedures. All other reagents were purchased from Aldrich, Sigma or Acros and used as received.

Instrumentation and measurements

¹H (500 and 400 MHz) and ¹³C{¹H} (125 and 100 MHz) NMR spectra were recorded on Bruker Avance AM 500 and Ascend 400 spectrometers at 25 °C. ¹H and ¹³C{¹H} NMR spectra were referenced internally relative to SiMe₄ (δ 0 ppm) using the residual solvent resonances.

Number-average molar mass (*M*_{n,SEC}) and dispersity (*D*_M = *M*_w/*M*_n) values of the PBPL^{FG}s were determined by size-exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL.min⁻¹) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μm MIXED-D 300 × 7.5

mm columns. The polymer samples were dissolved in THF (2 mg.mL⁻¹). All elution curves were calibrated with polystyrene standards; $M_{n,SEC}$ values of the PBPL^{FG}s were uncorrected for the possible difference in hydrodynamic radius vs. that of polystyrene.

The molar mass of PBPL^{FG} samples was also determined by ¹H NMR analysis in CDCl₃ from the relative intensities of the signals of the PBPL^{CH₂ZPh} repeating unit methine hydrogen (δ (ppm): 5.48 –OCH(CH₂OPh)CH₂, PBPL^{CH₂OPh}; 5.26 –OCH(CH₂SPh)CH₂, PBPL^{CH₂SPh}; 5.34 –OCH(CH₂CH₂OCH₂Ph)CH₂, PBPL^{CH₂CH₂OCH₂Ph}), and of the isopropyl chain-end (δ (ppm): 4.94–4.99 (CH₃)₂CHO–, 1.17–1.20 (CH₃)₂CHO–).

Monomer conversions were calculated from ¹H NMR spectra of the crude polymer samples in CDCl₃ by using the integration (Int.) ratios $\text{Int.PBPL(CH}_2\text{OPh) / PBPL(CH}_2\text{CH}_2\text{OCH}_2\text{Ph)} / [\text{Int.PBPL(CH}_2\text{OPh) / PBPL(CH}_2\text{CH}_2\text{OCH}_2\text{Ph)} + \text{Int.BPL(CH}_2\text{OPh) / BPL(CH}_2\text{CH}_2\text{OCH}_2\text{Ph)}]$, and $[\text{Int.PBPL(CH}_2\text{SPh)} + \text{Int.(2)} + \text{Int.(3)}] / [\text{Int.PBPL(CH}_2\text{SPh)} + \text{Int.BPL(CH}_2\text{SPh)} + \text{Int.(2)} + \text{Int.(3)}]$ (compounds **2** and **3** correspond to the decomposed and rearrangement products of *rac*-BPL^{CH₂SPh}, respectively; *vide infra*) of the methine hydrogens of BPL^{CH₂ZPh} and PBPL^{CH₂ZPh} (corresponding methine hydrogen signal of the polymers (see above), and of the monomers: δ (ppm) 4.85 BPL^{CH₂OPh}, 4.62 BPL^{CH₂SPh}, and 4.71 BPL^{CH₂CH₂OCH₂Ph}).

Mass spectra were recorded at CRMPO-ScanMAT (Rennes, France). ESI mass spectra were recorded on an orbitrap type Thermofisher Scientific Q-Exactive instrument with an ESI source in positive mode by direct introduction with a flow rate of 5–10 $\mu\text{L min}^{-1}$. Samples were prepared in CH₂Cl₂ at 10 $\mu\text{g mL}^{-1}$. High resolution Matrix Assisted Laser Desorption Ionization - Time of Flight, MALDI-ToF, mass spectra were recorded using an ULTRAFLEX III TOF/TOF spectrometer (Bruker Daltonik GmbH, Bremen, Germany) in positive ionization mode. Spectra were recorded using reflectron mode and an accelerating voltage of 25 kV. A mixture of a freshly prepared solution of the polymer in THF or CH₂Cl₂ (HPLC grade, 10 mg mL⁻¹) and DCTB (*trans*-2-(3-(4-*tert*-butylphenyl)-2methyl-2-propenylidene) malononitrile, and a MeOH solution of the cationizing agent (NaI, 10 mg mL⁻¹) were prepared. The solutions were combined in a 1:1:1 v/v/v ratio of matrix-to-sample-to-cationizing agent.

The resulting solution (0.25–0.5 μL) was deposited onto the sample target (Prespotted AnchorChip PAC II 384 / 96 HCCA) and air or vacuum dried.

Chiral HPLC analysis of (*S*) or (*R*)- G^{FG} s was performed on a Thermofisher Scientific chromatograph equipped with a Chiralcel-OD DAICEL column (250 mm $\times$ 4.6 mm, 5 μm) and a UV detector at 214 nm at 20 $^{\circ}\text{C}$, using for (*S*)- $\text{G}^{\text{CH}_2\text{OPh}}$: hexane/isopropanol 90:10 *v/v* (1 $\text{mL}\cdot\text{min}^{-1}$, 22 bar), (*S*)- $\text{G}^{\text{CH}_2\text{SPh}}$: hexane/isopropanol 99.5:0.5 *v/v* (0.9 $\text{mL}\cdot\text{min}^{-1}$, 23 bar), and (*R*)- $\text{G}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ (0.9 $\text{mL}\cdot\text{min}^{-1}$, 23 bar).

Thermal gravimetry analyses (TGA) were performed on a Metler Toledo TGA/DSC1 by heating the polymer samples at a rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ from +25 to +600 $^{\circ}\text{C}$ in a dynamic nitrogen atmosphere (flow rate = 50 $\text{mL}\cdot\text{min}^{-1}$).

Differential scanning calorimetry (DSC) analyses were performed with a Setaram DSC 131 apparatus calibrated with indium, at a rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$, under a continuous flow of helium (25 $\text{mL}\cdot\text{min}^{-1}$), using aluminum capsules. The thermograms were recorded according to the following cycles: –80 to 200 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$; 200 to –80 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$; –80 $^{\circ}\text{C}$ for 5 min; –80 to 200 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$; 200 to –80 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

Procedure for the carbonylation of the epoxides into the corresponding β -lactones¹⁷

Carbonylation of phenyl glycidyl ether (*rac*- $\text{G}^{\text{CH}_2\text{OPh}}$) into racemic 4-phenyloxymethylene- β -propiolactone (*rac*- $\text{BPL}^{\text{CH}_2\text{OPh}}$). In a typical experiment, in the glovebox, a Schlenk flask was charged with $[\text{Salph}(\text{Cr}(\text{THF})_2)][\text{Co}(\text{CO})_4]$ (235 mg, 0.26 mmol). On a vacuum line, dry DME (15 mL) was syringed in and the resulting solution was cannulated into a degassed high-pressure reactor, which was pressurized with carbon monoxide to 20 bars, and stirred for 15 min before depressurization. A solution of *racemic*-phenyl glycidyl ether (*rac*-2-(phenyloxymethyl)oxirane) (*rac*- $\text{G}^{\text{CH}_2\text{OPh}}$) (3.88 g, 25.9 mmol, 100 equiv.) in dry DME (15 mL) was transferred into the reactor, which was then pressurized with CO to 40 bars. The reaction mixture was stirred for 2 days at 20 $^{\circ}\text{C}$. The reactor was then vented to atmospheric pressure, volatiles were removed under vacuum and the crude product was purified through a silica column (CH_2Cl_2 , 2 $\times$ 300 mL). Evaporation of volatiles afforded *rac*- $\text{BPL}^{\text{CH}_2\text{OPh}}$

as a white solid that was crystallized from diethyl ether to give pure 4-phenoxyethylene- β -propiolactone (*rac*-BPL^{CH₂O^{Ph}}) (3.5 g; 75% yield). ¹H NMR (500 MHz, CDCl₃, 25 °C) δ (ppm): δ 7.34–7.28 (m, 2H_g), 7.03–6.98 (m, 1H_h), 6.95–6.91 (m, 2H_f), 4.88–4.81 (m, 1H_c), 4.33 (dd, J = 11, 3 Hz, 1H_e), 4.23 (dd, J = 11, 4 Hz, 1H_d), 3.62–3.53 (m, 2H_{ab}) (Figure S6-top). ¹³C NMR (125 MHz, CDCl₃, 25 °C) δ (ppm): 167.3 ($C_I=O$), 158.1 (*ipso*-C₅), 129.8 (*m*-C₇H), 121.9 (*p*-C₈H), 114.8 (*o*-C₆H), 68.4 (C₃HOC(O)), 67.4 (C₄H₂O^{Ph}), 40.2 (C₂H₂C(O)O) (Figure S6-bottom).

The carbonylation of (*S*)-phenyl glycidyl ether was performed similarly and gave (*S*)-BPL^{CH₂O^{Ph}} as an off-white solid (3.45 g, 74% yield) that displayed NMR spectra identical to those of *rac*-BPL^{CH₂O^{Ph}}.¹⁷ Both *rac*-BPL^{CH₂O^{Ph}} and (*S*)-BPL^{CH₂O^{Ph}} were stored under argon in the fridge at –27 °C.

Carbonylation of racemic 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂S^{Ph}}) to racemic 4-(phenylthio)methylene- β -propiolactone (*rac*-BPL^{CH₂S^{Ph}}). Following the aforementioned typical carbonylation procedure, starting from [Salph(Cr(THF)₂)] [Co(CO)₄] (218 mg, 0.24 mmol) and 2-((phenylthio)methyl)oxirane (*rac*-G^{CH₂S^{Ph}}) (4.0 g, 24 mmol, 100 equiv), *racemic* 4-(phenylthio)methylene- β -propiolactone (*rac*-BPL^{CH₂S^{Ph}}) was, following purification through a silica column using CHCl₃ as eluent followed by drying over 3–4 Å molecular sieves (thus avoiding distillation due to BPL^{CH₂S^{Ph}} instability), isolated as a pale yellow viscous liquid (2.4 g, 51% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): δ 7.45–7.40 (m, 2H_f), 7.36–7.24 (m, 3H_{g,h}), 4.63–4.55 (m, 1H_c), 3.50 (dd, J = 17, 6 Hz, 1H_d), 3.43 (dd, J = 14, 5 Hz, 1H_e), 3.17–3.11 (m, 2H_{ab}) (Figure S7-top). ¹³C NMR (101 MHz, CDCl₃, 25 °C) δ (ppm): 167.3 ($C_I=O$), 133.9 (*ipso*-C₅), 131.2 (*o*-C₆H), 129.4 (*m*-C₇H), 127.7 (*p*-C₈H), 68.9 (C₃HOC(O)), 43.0 (C₄H₂S^{Ph}), 38.0 (C₂H₂C(O)O) (Figure S7-bottom). ESI-MS m/z observed = 217.0293 vs m/z calculated = 217.0299 (Figure S8).

The carbonylation of (*S*)-G^{CH₂S^{Ph}} was performed similarly and gave (*S*)-BPL^{CH₂S^{Ph}} as a pale yellow viscous liquid (2.2 g, 47% yield) that displayed NMR spectra identical to those of *rac*-BPL^{CH₂S^{Ph}}. To prevent the degradation of *rac*-BPL^{CH₂S^{Ph}} and (*S*)-BPL^{CH₂S^{Ph}} (Figure S9),¹⁷ they were both freshly prepared prior to use.

Carbonylation of racemic 2-(2-(benzyloxy)ethyl)oxirane *rac*-G^{CH₂CH₂OCH₂Ph} to

racemic 4-(2-(benzyloxy)ethylene)- β -propiolactone (*rac*-BPL^{CH₂CH₂OCH₂Ph}).

Following the aforementioned typical carbonylation procedure, starting from [Salph(Cr(THF)₂)] [Co(CO)₄] (540 mg, 0.50 mmol) and *racemic* 2-(2-(benzyloxy)ethyl)oxirane (*rac*-G^{CH₂CH₂OCH₂Ph}) (8.9 g, 50 mmol, 100 equiv.), *racemic* 4-(2-(benzyloxy)ethylene)- β -propiolactone (*rac*-BPL^{CH₂CH₂OCH₂Ph}) was obtained as a colorless liquid (5.3 g, 52% yield) after evaporation of volatiles and purification through an alumina column using CHCl₃ as eluent. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ (ppm): 2.11 (m, 2H_d), 3.20 (dd, *J* = 16, 4 Hz, 1H_b), 3.53 (dd, *J* = 16, 6 Hz, 1H_a), 3.62 (td, *J* = 5, 2 Hz, 2H_e), 4.51 (s, 2H_f), 4.71 (m, 1H_c), 7.28-7.37 (m, 5H_g) (Figure S10-top); ¹³C NMR (125 MHz, CDCl₃, 25 °C) δ (ppm): 168.3 (C_I=O), 138.1 (*ipso*-C₇), 128.5 (*o*-C₈H), 127.8 (*o*-C₉H), 127.6 (*o*-C₁₀H), 73.2 (OC₆H₂Ph), 69.2 (C₃HCH₂CH₂O), 65.8 (CHCH₂C₅H₂O), 43.2 (C₂H₂C(O)O), 34.7 (CHC₄H₂CH₂O) (Figure S10-bottom). ESI-MS *m/z* observed=229.0836 vs *m/z* calculated = 229.0835 (Figure S11).

The carbonylation of (*R*)-G^{CH₂CH₂OCH₂Ph} was performed similarly and gave (*R*)-BPL^{CH₂CH₂OCH₂Ph} as a colorless liquid (1.5 g, 55% yield) that displayed NMR spectra identical to those of *rac*-BPL^{CH₂CH₂OCH₂Ph}. Both *rac*-BPL^{CH₂CH₂OCH₂Ph} and (*R*)-BPL^{CH₂CH₂OCH₂Ph} were stored under argon in fridge at -27 °C.

Typical polymerization procedure. In a typical experiment (Table 1, entry 6), in the glovebox, a Schlenk flask was charged with [Y(N(SiHMe₂)₂)₃](THF)₂ (8.8 mg, 14 μ mol) and {ONNO^{tBu2}} (**1d**, 7.4 mg, 14 μ mol), and toluene (0.25 mL) was next added. To this solution, *i*PrOH (107 μ L of a 1% (v/v) solution in toluene, 1 equiv vs. Y) was added under stirring at room temperature (ca. 20 °C). After 5 min of stirring, a solution of *rac*-BPL^{CH₂O^{Ph}} (150 mg, 0.84 mmol, 60 equiv) in toluene (0.5 mL) was added rapidly and the mixture was stirred at 20 °C for 1 h. The reaction was quenched by addition of acetic acid (ca. 0.5 mL of a 1.6 mol·L⁻¹ solution in toluene). The resulting mixture was concentrated to dryness under vacuum and the conversion was determined by ¹H NMR analysis of the residue in CDCl₃. The crude polymer was then dissolved in CH₂Cl₂ (ca. 1 mL) and precipitated in cold pentane (ca. 5 mL), filtered and dried. The PBPL^{CH₂O^{Ph}}, PBPL^{CH₂S^{Ph}} and PBPL^{CH₂CH₂OCH₂Ph} were recovered as white solid, yellow oil, and colorless oil, respectively. All recovered polymers were then analyzed by NMR spectroscopy,

mass spectrometry, SEC, TGA and DSC analyses (Table 1, Figures 1–5, S12–S25).

Results and discussion

The functional 4-substituted- β -propiolactones *rac*-BPL^{CH₂ZPh}_S and the enantiopure (*S*)- or (*R*)-BPL^{CH₂ZPh}_S (Z = O, S, CH₂OCH₂) were first prepared in good yields (47–75%) on a multi-gram scale (1.5–5.3 g) from the carbonylation reaction of the corresponding epoxide *rac*-, (*S*)- or (*R*)-G^{CH₂ZPh}_S, respectively, according to a typical procedure,¹⁷ and next characterized by NMR spectroscopy and mass spectrometry (MS) analyses (Figures S1–S11). While the synthesis of BPL^{CH₂O^{Ph}} was already reported,¹⁷ to our knowledge, its ring-opening homopolymerization has never been described. Only the random copolymerization of BPL^{CH₂O^{Ph}} with of BPL^{Me} via anionic simultaneous ring-opening copolymerization using the metal-free tetrabutylammonium acetate initiator was established to next study the resulting oligomers ($M_{n,SEC} = 1200 \text{ g mol}^{-1}$) by mass spectrometry.²³ In addition, for the first time to our knowledge, a functional β -lactone and PHA featuring a sulphur heteroatom within the exocyclic side-arm, namely BPL^{CH₂SPh} and PBPL^{CH₂SPh}, were prepared herein. Subsequently, the ROP of these original four-membered ring β -lactones was investigated, at room temperature in toluene, using the diamino- or amino-alkoxy-bis(phenolate) yttrium catalytic systems Y{ONXO^{R₂}}/(*i*PrOH) (**1a–1g**/(*i*PrOH)), the latter ones differing in terms of the phenolate *ortho*-substituents on the ancillary ligand (Scheme 2). Note that the influence of the *para*-substituents on the phenolate ligand of complexes **1** having been previously shown not to significantly contribute to the performance (especially the activity and the stereoselectivity) of the yttrium catalysts/initiators, they were not considered further in the present studies.^{12,15,16} These active catalysts were conveniently generated *in situ* upon addition of 1 equiv. of an exogeneous *i*PrOH, added as co-initiator to the mixture of the proligand and the yttrium amido precursor [Y(N(SiHMe₂)₂)₃](THF)₂, respectively (Scheme 2).^{15,16} The kinetics of the NMR-scale ROP of *rac*-BPL^{CH₂ZPh}_S was monitored by ¹H NMR spectroscopy. The most significant data for the thus synthesized PBPL^{CH₂ZPh}_S are gathered in Tables 1 and S1. The macromolecular characteristics, and especially the microstructure of the recovered PBPL^{CH₂ZPh}_S

polyesters, were thoroughly assessed by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and 2D (COSY, HMBC) NMR spectroscopy (Tables 1,S1; Figures S12–S18), MALDI-ToF MS (Figures S19–S21), SEC (Tables 1,S1), TGA and DSC (Table 1; Figures S22–S25) analyses.

Table 1. Characteristics of the PBPL^{CH₂ZPh}s synthesized by ROP of *rac*-BPL^{CH₂ZPh}s with Z = O, S, CH₂OCH₂ mediated by **1a–1g**/(*i*PrOH) catalytic systems in toluene at room temperature.

Entry	BPL ^{CH₂ZPh}	Cat.	[BPL ^{CH₂ZPh}] ₀ / [1] ₀ /[<i>i</i> PrOH] ₀ ^a	Time ^b (min)	Conv. ^c (%)	<i>M</i> _{n,theo} ^d (g.mol ⁻¹)	<i>M</i> _{n,NMR} ^e (g.mol ⁻¹)	<i>M</i> _{n,SEC} ^f (g.mol ⁻¹)	<i>D</i> _M ^f	<i>P</i> _r ^g	<i>T</i> _g ^h (°C)
1	CH ₂ OPh	1a	30:1:1	120	100	5400	5200	6200	1.18	0.76	<i>nd</i> ⁱ
2 ⁱ	CH ₂ OPh	1a	60:1:1	240	95	10 200	10 000	11 100	1.13	0.79	30
3	CH ₂ OPh	1c	30:1:1	30 h	95	5100	5000	5200	1.14	0.77	22
4 ⁱ	CH ₂ OPh	1c	60:1:1	50 h	54	5800	5400	6200	1.15	0.75	21
5	CH ₂ OPh	1d	20:1:1	120	100	3600	3200	4100	1.21	0.84	<i>nd</i> ⁱ
6 ⁱ	CH ₂ OPh	1d	60:1:1	8	100	10 700	10 600	12 200	1.14	0.86	37
7	CH ₂ OPh	1d	120:1:1	8	98	21 000	23 000	25 600	1.06	0.86	37
8	CH ₂ OPh	1d	250:1:1	15	100	44 600	44 100	51 200	1.16	0.87	38
9	CH ₂ OPh	1d	500:1:1	15	92	81 900	80 500	95 000	1.20	0.86	40
10	CH ₂ OPh	1f	28:1:1	120	100	5000	4700	5400	1.20	0.81	<i>nd</i> ⁱ
11 ⁱ	CH ₂ OPh	1f	60:1:1	30	100	10 700	10 000	12 200	1.15	0.84	38
12	CH ₂ OPh	1f	100:1:1	8	100	17 900	17 800	19 000	1.11	0.83	40
13	(<i>S</i>)-CH ₂ OPh	1d	60:1:1	60	100	10 700	10 500	11 700	1.10	<0.05	36
14	CH ₂ SPh	1a	30:1:1	240	100	5900	5800	6600	1.14	0.74	9
15 ⁱ	CH ₂ SPh	1a	60:1:1	480	99	11 600	11 300	13 900	1.21	0.76	8
16	CH ₂ SPh	1c	20:1:1	240	38	1500	1 400	1700	1.08	<i>nd</i> ⁱ	<i>nd</i> ⁱ
17	CH ₂ SPh	1c	30:1:1	60 h	57	3400	3400	3600	1.14	0.73	9
18 ⁱ	CH ₂ SPh	1c	60:1:1	96 h	48	5600	5100	6400	1.17	0.74	9
19	CH ₂ SPh	1d	40:1:1	240	100	7800	7400	8900	1.19	0.83	<i>nd</i> ⁱ
20 ⁱ	CH ₂ SPh	1d	80:1:1	60	100	15 600	15 200	17 900	1.15	0.87	13
21	CH ₂ SPh	1d	120:1:1	15	100	23 200	23 300	25 700	1.07	0.86	14
22	CH ₂ SPh	1d	250:1:1	60	95	46 100	48 300	51 400	1.15	0.87	14
23	CH ₂ SPh	1d	500:1:1	120	90	87 400	86 400	96 700	1.17	0.86	12
24	CH ₂ SPh	1f	20:1:1	60	100	3900	3400	4400	1.19	0.85	<i>nd</i> ⁱ
25 ⁱ	CH ₂ SPh	1f	60:1:1	60	100	11 700	11 300	13 300	1.12	0.85	13
26	CH ₂ SPh	1f	120:1:1	15	95	22 200	23 200	24 600	1.14	0.84	12

27	(S)-CH ₂ SPh	1d	60:1:1	60	100	11 700	11 500	12 800	1.13	<0.05	13
28	CH ₂ CH ₂ OCH ₂ Ph	1a	50:1:1	9 h	67	7000	8600	7000	1.23	0.49	–12
29	CH ₂ CH ₂ OCH ₂ Ph	1b	25:1:1	7.5 h	99	5200	5400	4300	1.48	0.49	<i>nd</i> ^d
30	CH ₂ CH ₂ OCH ₂ Ph	1b	50:1:1	9 h	87	9000	9550	8000	1.06	0.52	<i>nd</i> ^d
31	CH ₂ CH ₂ OCH ₂ Ph	1c	25:1:1	14 h	78	4100	5200	4200	1.15	0.49	–15
32	CH ₂ CH ₂ OCH ₂ Ph	1d	25:1:1	5	99	5200	6400	6700	1.12	0.85	–11
33	CH ₂ CH ₂ OCH ₂ Ph	1e	25:1:1	5	99	5200	5100	6800	1.21	0.80	–13
34	CH ₂ CH ₂ OCH ₂ Ph	1f	25:1:1	3	99	5200	5400	4400	1.09	0.77	–12
35	CH ₂ CH ₂ OCH ₂ Ph	1f	100:1:1	10	98	20 200	-	19 200	1.05	0.77	<i>nd</i> ^d
36	CH ₂ CH ₂ OCH ₂ Ph	1g	25:1:1	3	99	5200	6600	5400	1.19	0.86	–13
37	CH ₂ CH ₂ OCH ₂ Ph	1g	50:1:1	3	99	10 300	-	8500	1.12	0.81	<i>nd</i> ^d
38	CH ₂ CH ₂ OCH ₂ Ph	1g	100:1:1	6	99	20 500	-	20 600	1.07	0.85	–9
39	CH ₂ CH ₂ OCH ₂ Ph	1g	150:1:1	15	99	31000	-	29800	1.08	0.82	<i>nd</i> ^d
40	(R)-CH ₂ CH ₂ OCH ₂ Ph	1d	50:1:1	10	99	10 300	9100	8400	1.15	<0.05	–14

^a Reactions performed with [BPL^{CH₂ZPh}]₀ = 1.0 M. ^b Reaction time was not necessarily optimized. ^c Conversion of BPL^{CH₂ZPh} as determined by ¹H NMR analysis of the crude reaction mixture. ^d Molar mass calculated according to $M_{n,theo} = ([BPL^{CH_2ZPh}]_0/[1]_0 \times \text{conv.}_{BPL(CH_2ZPh)} \times M_{BPL(CH_2ZPh)}) + M_{iPrOH}$, with $M_{BPL(CH_2OPh)} = 178 \text{ g.mol}^{-1}$, $M_{BPL(CH_2SPh)} = 194 \text{ g.mol}^{-1}$, $M_{BPL(CH_2CH_2OCH_2Ph)} = 206 \text{ g.mol}^{-1}$, $M_{iPrOH} = 60 \text{ g.mol}^{-1}$. ^e Molar mass determined by ¹H NMR analysis of the isolated polymer, from the resonances of the terminal OiPr group (refer to Experimental section). ^f Number-average molar mass and dispersity (M_w/M_n) determined by SEC analysis in THF at 30 °C vs. polystyrene standards. ^g P_r is the probability of *racemic* linkages between BPL^{CH₂ZPh} units as determined by ¹³C{¹H} NMR analysis of the isolated PBPL^{CH₂ZPh}s. ^h Glass transition temperature as determined by DSC. ⁱ Refer to the kinetic study (Table S1); ^j Not determined.

ROP of *rac*-BPL^{CH₂ZPh}s (Z = O, S, CH₂OCH₂) promoted by **1a–1g**/(*i*PrOH) catalyst systems: insights into the catalyst activity and the kinetics

Yttrium catalyst systems based on ligands with small Me or Cl *ortho*-phenolate substituents (**1a–1c**), in the presence of *i*PrOH, proved poorly active regardless of the *rac*-BPL^{CH₂ZPh}, presumably due to the aggregated/dimeric nature of these metal complexes (Table 1, entries 1–4,14–18,28–31).^{8b} The Me-substituted catalyst systems **1a,1b**/(*i*PrOH) could achieve near complete conversion of ca. 30 monomer equiv. in a few hours (99–100% yield, i.e. 25–30 equiv. in 2–7.5 h), unlike the Cl-substituted one **1c** which hardly proceeded to complete monomer consumption (57–95% yield, i.e. 17–28 equiv. in 14–60 h) (Table 1, entries 1,14,29;3,17,31). Correspondingly, the best activity achieved by the catalysts as expressed by turnover frequency (TOF) values remained sluggish: TOF_{1a-b} = 4.8–15 h^{–1} vs TOF_{1c} = 1.0–1.4 h^{–1} (Table 1, entries

2,15,30;3,16,30). This poor activity of uncrowded alkyl or halogenated catalysts **1a–1c**/(*i*PrOH) contrasted with the moderate-to-high activity recorded in the alike ROP of BPL^{CH₂OAll/Bn} (TOF = 20–30 h^{–1}) or BPL^{CO₂R} (TOF = 1400 h^{–1}) under the same operating conditions.^{8b,15,16} On the other hand, yttrium catalyst systems with ancillary ligands bearing bulky substituents (*t*Bu, cumyl, **1d–1g**/(*i*PrOH)) revealed quite active for the ROP of *rac*-BPL^{CH₂ZPh}s, with the cumyl substituted derivatives being most efficient (Table 1, entries 5–13,19–27,32–40). Nearly quantitative conversion of ca. 98–120 equivalents of *rac*-BPL^{CH₂ZPh} by **1d–1g** was reached within 6–15 min (Table 1, entries 7,12,21,26,35,38). The overall slightly faster rate of polymerization observed for BPL^{CH₂O^{Ph}} as compared to BPL^{CH₂SPh} (Tables 1,S1; Figure 1), regardless of the catalytic system, most likely arose from the relative instability of BPL^{CH₂SPh} at 20 °C, the secondary products formed (products **2** and **3**; Figure S9) presumably impeding the efficiency of the catalyst, hence altering the polymerization rate. Furthermore, the highest TOF values obtained for the ROP of BPL^{CH₂O^{Ph}/CH₂SPh/CH₂CH₂OCH₂Ph} promoted by the catalytic systems **1d–1g**/(*i*PrOH) (450 < TOF (h^{–1}) < 1840; Table 1, entries 7,9,12,21,26,34–39) were significantly higher than those reported for the closely related alkoxymethylene β-propiolactones BPL^{CH₂OR}s (R = Me, Bn, All) similarly polymerized by these same yttrium catalytic systems (TOF = 54–100 h^{–1}),^{8b,16} yet lower than those obtained from BPL^{CO₂R} monomers with pendant ester side-chains (R = Bn, All; TOF > 3000 h^{–1}).^{15b} The overall trend for the monomers' ROP ability is thus BPL^{CH₂O^{Ph}} ≈ BPL^{CH₂SPh} > BPL^{CH₂CH₂OCH₂Ph}, while the catalysts' activity thus generally followed the order **1d–1g** >> **1a** ≈ **1b** >> **1c**, as previously reported for the previous ROP of various BPL^{FG}s β-lactones (FG = Me, CH₂OR, CO₂R) promoted by these catalyst systems.^{7,15,16}

Monitoring of NMR-scale polymerizations of BPL^{CH₂O^{Ph}/CH₂SPh/CH₂CH₂OCH₂Ph} performed with **1a–1g**/(*i*PrOH) confirmed the kinetics trend derived from batch experiments, and linear semi-logarithmic plots established that all reactions were first order in monomer (apparent rate constant k_{app} = 67.3 ± 3.1 min^{–1}, BPL^{CH₂CH₂OCH₂Ph}/**1d**; 32.93 ± 0.01 min^{–1}, BPL^{CH₂O^{Ph}/CH₂SPh}/**1d,1f**; 15.05 ± 0.38 min^{–1}, BPL^{CH₂CH₂OCH₂Ph}/**1f**; 0.76 ± 0.07 min^{–1}, BPL^{CH₂O^{Ph}}/**1a**; 0.58 ± 0.11 min^{–1}, BPL^{CH₂SPh}/**1a**; 9.05 ± 0.06 × 10^{–2} min^{–1}, BPL^{CH₂O^{Ph}}/**1c**; 6.69 ± 0.62 × 10^{–2} min^{–1}, BPL^{CH₂CH₂OCH₂Ph}/**1a**;

$4.25 \pm 0.43 \times 10^{-2} \text{ min}^{-1}$, $\text{BPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}/\mathbf{1c}$; $1.2 \pm 0.1 \times 10^{-2} \text{ min}^{-1}$, $\text{BPL}^{\text{CH}_2\text{SPh}}/\mathbf{1c}$
(Tables 1,S1, Figure 1).

Figure 1. Semi-logarithmic first-order plots for the ROP of *rac*-BPL^{FG}s mediated by **1a**, **1c**, **1d**, **1f**/(*i*PrOH) (20 °C, toluene; $[\text{BPL}^{\text{CH}_2\text{ZPh}}]_0/[\mathbf{1}]_0/[i\text{PrOH}]_0 = 60:1:1$): **1a** (Table 1, entries 2,15; Table S1, entry 1); **1c** (Table 1, entries 4,18; Table S1, entry 2); plots for the ROPs mediated by **1d** (Table 1, entries 6,20; Table S1, entry 3) and **1f** (Table 1, entries 11,25; Table S1, entry 4), all overlap due to similar high activity of these catalysts regardless of the monomer, and are represented as ▲.

All the PBPL^{CH₂ZPh}s isolated showed, regardless of the catalytic system used, a quite good agreement between the theoretical molar mass values ($M_{n,\text{theo}}$) and the experimental values determined by NMR ($M_{n,\text{NMR}}$) and by SEC ($M_{n,\text{SEC}}$) analyses. The latter experimental molar mass values of the PBPL^{CH₂ZPh}s increased linearly with the BPL^{CH₂ZPh} monomer loading up to a degree of polymerization of ca. 450, as illustrated for the ROP of BPL^{CH₂ZPh} mediated by the **1d** or **1g**/(*i*PrOH) (1:1) catalytic system (Figure 2; Table S1). The dispersities of all PBPL^{CH₂ZPh}s remained generally narrow

($\bar{D}_M = 1.05$ – 1.23), supporting a relatively fast initiation (compared to propagation) along with some limited undesirable side reactions (classically inter- and intra-molecular transesterification reactions (i.e. reshuffling and backbiting, respectively), or other transfer or termination reactions). Such dispersity values fell within the range of those typically obtained for the related *racemic* 4-substituted- β -propiolactones BPL^{FG}s.^{8,15,16} All these characteristics highlighted the controlled feature and to some extent the livingness of the ROP of the BPL^{CH₂ZPh}s mediated by **1a–1g**/(*i*PrOH) catalytic systems.

Figure 2. Variation of $M_{n,NMR}$ ■, $M_{n,SEC}$ ●, and $M_{n,theo}$ (solid line) values of PBPL^{CH₂ZPh}s synthesized from the ROP of *rac*-BPL^{CH₂ZPh}s mediated by **1d** or **1g**/(*i*PrOH) (1:1) catalytic system as a function of the BPL^{CH₂ZPh} monomer loading (Table 1, entries 5–9;19–23;36–39).

Macromolecular characterizations of PBPL^{CH₂ZPh}s synthesized by ROP of *rac*-BPL^{CH₂ZPh}s (Z = O, S, CH₂OCH₂) promoted by **1a–1g**/(*i*PrOH) catalyst systems

The PBPL^{CH₂ZPh}s were unambiguously characterized by 1D and 2D NMR spectroscopy and mass spectrometry (Tables 1,S1; Figures 3–5,S12–S18). All ¹H and ¹³C{¹H} and J-MOD NMR spectra clearly displayed the characteristic signals corresponding to both the BPL^{CH₂ZPh} repeating units, especially the backbone methine and methylene signals, and the typical pendant CH₂ZPh moieties, respectively (refer to the Experimental Section). The distinctive isopropoxycarbonyl chain-end group resonances were also clearly observed (δ (ppm): ca. 4.95 (CH₃)₂CHO–, ca. 1.19 (CH₃)₂CHO–), supporting the propagation from the Y{ONXO^{R2}}/(*i*PrOH) active species (Figures 3–5,S12–S18).

Further support of the macromolecular structure of the PBPL^{CH₂ZPh}s was gained from ESI or MALDI-ToF mass spectrometry analyses (Figures S19–S21). The spectra recorded for low molar mass samples of PBPL^{CH₂ZPh}s prepared from **1d,1f**/iPrOH catalytic systems, showed a single population of macromolecules having a repeating unit of *m/z* 178, 194, or 206 (*M*_{BPL(CH₂OPh)}, *M*_{BPL(CH₂SPh)}, *M*_{BPL(CH₂CH₂OCH₂Ph)}), respectively, corresponding to α-isopropoxy, ω-hydroxyl telechelic PBPL^{CH₂ZPh} chains ionized by Na⁺. This was unequivocally confirmed by the close match with the corresponding isotopic simulations, as illustrated for [(CH₃)₂CHO(COCH₂CH(CH₂OC₆H₅)O)_{*n*}H]·Na⁺ with, for example, calculated *m/z* 1507.551 versus found *m/z* 1507.548 for *n* = 8 (PBPL^{CH₂OPh}), for [(CH₃)₂CHO(COCH₂CH(CH₂SC₆H₅)O)_{*n*}H]·Na⁺ with, for example, calculated *m/z* 1053.2475 versus found *m/z* 1053.2473 for *n* = 5 (PBPL^{CH₂SPh}), and for [(CH₃)₂CHO(COCH₂CH(CH₂CH₂OCH₂C₆H₅)O)_{*n*}H]·Na⁺ with, for example, calculated *m/z* 3174.493 versus found *m/z* 3174.461 for *n* = 15 (PBPL^{CH₂CH₂OCH₂Ph}). Note that the second population observed in the MALDI-ToF mass spectrum of PBPL^{CH₂CH₂OCH₂Ph} corresponds to α-isopropoxy, ω-dehydrated (i.e., ω-crotonate) telechelic PBPL^{CH₂CH₂OCH₂Ph} chains ionized by Na⁺, as unambiguously confirmed by the close match with the corresponding isotopic simulation for [(CH₃)₂CHO(COCH₂CH(CH₂CH₂OCH₂C₆H₅)O)_{*n*}H–H₂O]·Na⁺ with, for example, calculated *m/z* 3156.476 versus found *m/z* 3156.451 for *n* = 15. However, such a crotonate group was not detected in the NMR spectra of the prepared PBPL^{CH₂CH₂OCH₂Ph}s (no signals observed at δ_{1H} 6.25, 5.77 ppm (CH=CHCH₂CH₂OCH₂Ph)), thus suggesting that the dehydration of the macromolecular chains occurred during the MALDI-ToF MS analysis or that it is a very minor population.

Figure 3. ¹H NMR (500 MHz, CDCl₃, 25 °C) (top) and J-MOD (125 MHz, CDCl₃, 25 °C) (bottom) spectra of syndiotactic PBPL^{CH₂OPh} prepared from the ROP of *rac*-BPL^{CH₂OPh} mediated by complex **1d** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 6) (*: residual grease).

Figure 4. ¹H NMR (500 MHz, CDCl₃, 25 °C) (top) and J-MOD (125 MHz, CDCl₃, 25 °C) (bottom) spectra of syndiotactic PBPL^{CH₂SPh} prepared from the ROP of *rac*-BPL^{CH₂SPh} mediated by complex **1f** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 26) (*: minor peaks correspond to the degradation product **3** of BPL^{CH₂SPh}).

Figure 5. ^1H NMR (500 MHz, CDCl_3 , 25 °C) (top) and J-MOD (100 MHz, CDCl_3 , 25 °C) (bottom) spectra of syndiotactic $\text{PBPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ prepared from the ROP of $\text{rac-BPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$ mediated by complex **1b** in the presence of *i*PrOH and precipitated twice in cold pentane (Table 1, entry 29).

Microstructural characterization of $\text{PBPL}^{\text{CH}_2\text{ZPh}}$ s: Stereoselectivity of the catalysts **1a–1g**/*i*PrOH in the ROP of $\text{rac-BPL}^{\text{CH}_2\text{ZPh}}$ s (Z = O, S, CH_2OCH_2)

Motivated by the outstanding stereoselectivity of the achiral $\text{Y}\{\text{ONXO}^{\text{R}_2}\}/(\text{iPrOH})$ catalyst systems **1a–1g**/*i*PrOH in the ROP of chiral β -lactones,^{8a,8b,15,16} the stereoregularity of the herein synthesized $\text{PBPL}^{\text{CH}_2\text{ZPh}}$ s was closely examined. Most commonly, the stereocontrol in the ROP of chiral cyclic esters mediated by achiral metal catalyst systems originates from a so-called chain-end stereocontrolled mechanism (CEM) in which the chirality of each next incoming monomer unit is tuned by the chirality of the last monomer unit inserted into the growing polymer chain.⁸ Thus, syndiotactic polymers are most often formed from CEM, since the active species

alternatively selects from a *racemic* monomer, the enantiomer with the opposite configuration in order to minimize the steric bulkiness in the transition state.

The tacticity of the recovered PBPL^{CH₂ZPh}_s was thus assessed from ¹³C NMR spectra analyses (upon comparison with the corresponding spectra of the isotactic PBPL^{CH₂ZPh}_s synthesized from the enantiopure monomers, respectively (Figures S12–14,S18)) in close relationship with the nature of the exocyclic side-chain and the nature of the substituted phenolate ligand framework of the yttrium complexes **1a–1g**/(*i*PrOH) (Figure 6, Table 1). It is worth pointing out that the *rac*-BPL^{CH₂ZPh}_s (Z = O, S, CH₂OCH₂) herein investigated “simply” differ from the previously studied *rac*-BPL^{CH₂OCH₂Ph} by one less methylene group in the phenoxide/phenylthiol moiety in the case of BPL^{CH₂O^{Ph}} and BPL^{CH₂S^{Ph}}, or by the replacement in the exocyclic pendant group of a methylene by an ethylene moiety in the case of BPL^{CH₂CH₂OCH₂Ph}. The stereoselectivity of the yttrium catalysts incorporating variously *ortho*-substituted phenolate ligands revealed different from one class of BPL^{FG} monomer to another; the stereoselectivity was strongly affected by the nature of the R *ortho*-substituents installed on the phenolate ligands and by the nature of the exocyclic functional group FG of the β-lactone monomer (Tables S2,S3).

First, no significant difference in terms of stereoselectivity of PBPL^{CH₂ZPh}_s was observed to arise from the X donor group in the “capping” moiety of the {ONXO^{R₂}}^{2–} ligand, similarly to the previous alike ROP of BPL^{FG}_s with FG = Me, CH₂OR, C(O)OR.⁸ Regardless of the catalyst system implemented, exchanging oxygen with sulphur in FG = CH₂ZPh (Z = O, S, i.e. BPL^{CH₂O^{Ph}} vs BPL^{CH₂S^{Ph}}) did not affect the stereochemistry of the resulting syndiotactic PBPL^{CH₂ZPh}_s. This was different with PBPL^{CH₂CH₂OCH₂Ph} which revealed either syndiotactic or atactic, depending on the yttrium complex used, namely **1d–1g** or **1a–1c**, respectively. Generally, ¹³C NMR spectra of the PBPL^{CH₂ZPh}_s indicated that when the yttrium complex incorporated bulky substituents at the *ortho*-positions of the phenolate rings (*t*Bu or cumyl groups, **1d–1g**), syndio-enriched PBPL^{CH₂ZPh}_s (*P_r* up to 0.77–0.87) were produced from *rac*-BPL^{CH₂ZPh}_s, (Table 1, entries 5–12,19–26,32–39). In comparison, similarly highly syndiotactic PBPL^{CH₂OCH₂Ph}_s were reported from *rac*-BPL^{CH₂OCH₂Ph} (*P_r* = 0.88–0.90).^{16a}

Unexpectedly and most strikingly, the use of an *ortho*-dichloro-substituted ligand in **1c** gave syndio-enriched PBPL^{CH₂OPh/CH₂SPh} ($P_r = 0.73$ – 0.77) (Table 1, entries 3,4,17,18) and atactic PBPL^{CH₂CH₂OCH₂Ph} ($P_r = 0.49$) (Table 1, entry 31), in comparison to isotactic PBPL^{CH₂OCH₂Ph} ($P_r = 0.10$).^{16a} Also, while the similarly uncrowded *ortho*-dimethyl-substituted ligand in **1a–1b** returned, similarly to the dichloro analogue **1c**, syndio-enriched PBPL^{CH₂OPh/CH₂SPh} ($P_r = 0.74$ – 0.79) (Table 1, entries 1,2,14,15) and atactic PBPL^{CH₂CH₂OCH₂Ph} ($P_r = 0.49$ – 0.52) (Table 1, entry 28–30), it afforded atactic PBPL^{CH₂OCH₂Ph} ($P_r = 0.50$)^{16a} and atactic PBPL^{Me} ($P_r = 0.56$).¹² Methylene groups apart from the exocyclic oxygen of the side-arm or a simple methyl substituent thus appeared detrimental to the stereoselectivity control promoted by uncrowded **1a–1c** catalysts.

The stereochemistry of the PBPL^{CH₂ZPh}s reported herein can be more largely compared to that of all the previously reported PBPL^{FG}s (FG = Me, CH₂OR, CO₂R with R = Me, All, Bn) similarly prepared by ROP of BPL^{FG} promoted by **1a–1g**/(*i*PrOH), as summarized in Tables S2,S3.^{15,16} Considering the catalyst system based on **1c** flanked with an halogenated non-crowded ancillary ligand, the presence of two “CH₂” moieties apart from the central oxygen of the pendant FG = CH₂OR (R = Me (CH₃), All (CH₂CH=CH₂), Bn (CH₂Ph)), i.e. “CH₂OCH₂” in 4-alkoxymethylene-β-propiolactones BPL^{CH₂OR}s, was evidenced to be essential to afford highly isotactic PBPL^{CH₂OMe/All/Bn}s that arose from the presence of strong Cl...C–H non-covalent interactions (NCIs) between the chloro substituents and the two methylene groups.¹⁶ The stereocontrol was then switched to syndiotacticity, either upon replacement of one of these methylenes into FG = C(O)OR of the β-malolactonates, or upon its removal into FG = CH₂OPh or CH₂SPh of the BPL^{CH₂ZPh}s (Z = O, S). Moreover, increasing the length of the pendent chain from alkoxymethylene “CH₂OCH₂” in BPL^{CH₂OR}s to alkoxyethylene “CH₂CH₂OCH₂” in BPL^{CH₂CH₂OCH₂Ph} seem to affect the Cl...CH₂s interactions. We assume this is possibly due to a different conformation in the monomer/active species interactions, and/or due to the decrease in acidity of the methine-adjacent methylenes of the side-chain in –CH₂CH₂OCH₂Ph vs –CH₂OCH₂Ph, ultimately weakening the NCIs and leading to the loss of stereocontrol to afford atactic polymers, similarly to those obtained with BPL^{Me}.^{12b,c}

The ROP of the β -lactones promoted by non-crowded non-halogenated yttrium catalysts, typically Me-substituted phenolate catalysts **1a–1b**, provided atactic PBPL^{FG}s, except with BPL^{CH₂OPh/CH₂SPh} and the β -malolactonate monomers¹⁵ which returned syndio-enriched-to-highly syndiotactic polymers, respectively. This latter stereocontrol might then originate from the coordination to the yttrium center of the heteroatom (O, S) atom of the phenoxide (CH₂OPh), thiophenoxide (CH₂SPh) or alkoxycarbonyl (C(O)OR) of the side-group of the last inserted monomer unit of the growing chain, thereby forming a highly coordinated – and thus bulkier and more prone to stereoselectivity – rare earth active species.

Finally, when implementing crowded substituted phenolate ligands, *i.e.* CMe₂Ph and *t*Bu, onto the yttrium active center **1d–1g**/(*i*PrOH), syndiotactic polymers were commonly produced regardless of the BPL^{FG} exocyclic substituent (FG = Me, CH₂OPh, CH₂SPh or CH₂CH₂OCH₂Ph, CO₂All/Bn, CH₂OMe/All/Bn), in line with a CEM mechanism being at play. The results we report herein thus further highlight the strong dependence of the resulting PHA's stereocontrolled microstructure on the couple formed by the functional β -lactone and the yttrium catalyst, and more specifically on the chemical nature of the β -lactone side-arm and of the substituents on the metal surrounding ancillary.

Figure 6. Regions of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (125 MHz, CDCl_3 , 23 °C) of PBPL^{CH₂ZPh}s prepared by ROP of *rac*-BPL^{CH₂ZPh}s (Z = O, S, CH₂OCH₂), except for the

top spectra: of enantiopure (*S* or *R*)-BPL^{CH₂ZPh}) (Table 1, entries 13,27,40), mediated by **1a**, **1c**, **1d**, or **1f** /(iPrOH): (left) PBPL^{CH₂O^{Ph}} (Table 1, entries 2,4,6,9), (middle) PBPL^{CH₂SPh} (Table 1, entries 15,18,20,25), (right) PBPL^{CH₂CH₂OCH₂Ph} (Table 1, entries 28,31,32,34).

Thermal characteristics of PBPL^{CH₂ZPh}s synthesized by ROP of *rac*-BPL^{CH₂ZPh}s (Z = O, S, CH₂OCH₂) promoted by **1a–g catalyst systems**

The thermal behavior of the synthesized PBPL^{CH₂ZPh}s was analyzed by thermal gravimetry analysis (TGA) and differential scanning calorimetry (DSC) (Figures S22–S25). The PBPL^{CH₂O^{Ph}} and PBPL^{CH₂SPh} samples were found to thermally degrade at the same temperature ($T_d^{\text{onset}}_{\text{PBPLCH}_2\text{O}^{\text{Ph}}} = 272\text{ }^\circ\text{C}$, $T_d^{\text{onset}}_{\text{PBPLCH}_2\text{SPh}} = 271\text{ }^\circ\text{C}$) that is significantly higher than the one measured for PBPL^{Me} ($T_d^{\text{onset}} = 256\text{ }^\circ\text{C}$) and PBPL^{CH₂CH₂OCH₂Ph} ($T_d^{\text{onset}}_{\text{PBPLCH}_2\text{CH}_2\text{OCH}_2\text{Ph}} = 226\text{ }^\circ\text{C}$) (Figure S22). DSC thermograms only showed the presence of a glass transition temperature (T_g); no melting temperature was observed below 200 °C, suggesting amorphous polyesters (Tables 1,S2,S3; Figures S23–S25). This lack of crystallinity was similarly reported for the closely related syndiotactic or isotactic PBPL^{CH₂OCH₂Ph}, while a melting temperature was only observed for the syndiotactic PBPL^{CH₂OMe/All} ($T_m = 116, 85\text{ }^\circ\text{C}$) and PBPL^{CO₂All/Bn} ($T_m = 51\text{--}117\text{ }^\circ\text{C}$).^{15b,16a} The T_g values were similarly observed to be closely related to the nature of the functional side-chain of the PHAs. The PBPL^{CH₂O^{Ph}/CH₂SPh} displayed positive T_g values going from 8 to 14 °C for the phenoxymethylene substituent, up to 21 to 40 °C for the corresponding thiophenoxymethylene. On the other hand, the PBPL^{CH₂CH₂OCH₂Ph} polyester with the longer benzyloxyethylene pendant moieties, that most likely impart more mobility to the macromolecular chains, showed the lowest T_g (typically $T_g = -12\text{ }^\circ\text{C}$) – and T_d as well – values.

The influence of the stereoenrichment of PBPL^{CH₂ZPh}s on T_g showed, as anticipated, higher T_g values for the most syndiotactic polymers as compared to the less syndio-enriched ones (Tables 1, S1; Figures S23–S25). Typically, for PBPL^{CH₂O^{Ph}}s with $P_r = 0.75\text{--}0.79$, the T_g values varied from 21 to 30 °C, while a higher syndio-enrichment with $P_r = 0.83\text{--}0.87$ or an almost purely isotactic sample ($P_r < 0.05$) resulted in higher

T_g values ranging from 36 to 40 °C. The same trend was observed with PBPL^{CH₂SPh}_s that displayed T_g values varying from 8–9 °C for samples with $P_r = 0.73$ – 0.76 , while more syndio-enriched polymer samples with $P_r = 0.83$ – 0.87 or an almost purely isotactic sample ($P_r < 0.05$) gave higher T_g values ranging from 12 to 14 °C. The trend is, as expected, similar to the previously reported thermal behavior of the related PBPL^{CH₂OCH₂Ph} that showed a T_g value going from –6 °C to –2 and to 0 °C upon improving the stereoregularity of the polyesters from atactic (P_r ca. 0.50) to syndiotactic (P_r ca. 0.85–0.90) and isotactic (P_r ca. 0.10), respectively.¹⁶ No distinct tendency in the T_g values of PBPL^{CH₂CH₂OCH₂Ph} samples was however observed.

Conclusion

The unprecedented functional PBPL^{CH₂ZPh}_s with Z = O, S, CH₂OCH₂ have been easily and successfully prepared from the controlled ROP of the corresponding *racemic* 4-substituted- β -propiolactones *rac*-BPL^{CH₂ZPh}_s, mediated by diamino- or amino-alkoxy-bis(phenolate) yttrium amido complexes **1a–1g** in the presence of isopropanol as co-initiator. All yttrium complexes revealed active, affording well-defined high molar mass PHAs with a good control of the polymerization in terms of molar mass values and limited undesirable side reactions ($M_{n,NMR}$ up to 86,400 g mol^{–1}, $\mathcal{D}_M < 1.23$).

The best activities reached by the yttrium complexes **1d–1g** with the most crowded substituents installed on the tetradentate bisphenolate ligand (e.g. *t*Bu, CMe₂Ph), in the ROP of these β -lactones (typically $225 < \text{TOF (h}^{-1}) \leq 1840$), revealed significantly higher than those achieved with the related *rac*-4-alkoxymethylene- β -propiolactones BPL^{CH₂OMe/Al/Bn} ($1 < \text{TOF (h}^{-1}) < \text{ca. } 100$),¹⁶ yet lower than the record value established with the ROP of *rac*- β -malolactonates BPL^{CO₂R} ($\text{TOF} \geq 3000 \text{ h}^{-1}$).¹⁵ On the other hand, catalysts with less-crowded phenolate substituents (e.g. Me, Cl) revealed significantly less active in the ROP of *rac*-BPL^{CH₂ZPh}_s, with the chloro derivative **1c** being sluggish, as previously observed in the ROP of BPL^{CH₂OAl/Bn}.^{8b}

Highly *syndiotactic* PBPL^{CH₂OPh} and PBPL^{CH₂SPh}_s were always obtained (P_r up to 0.87), unrelatedly to the O or S heteroatom and regardless of the yttrium catalyst, and similarly to syndiotactic PBPL^{Me}, PBPL^{CH₂OMe/Al/Bn}, and PBPL^{CO₂Al/Bn}.^{8,12,15,16} On the

other hand, the simple modification of *ortho*-R substituents on the $\{\text{ONOO}^{\text{R}_2}\}^{2-}$ ligand platform from uncrowded to crowded, allowed a complete reversal from a *nonselective* (P_r ca.0.50 with R = Cl, Me) to highly *syndioselective* (P_r up to 0.86 with R = cumyl, *ter*-butyl) ROP of $\text{BPL}^{\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}}$, respectively. The intimate relationship between the chemical nature of the exocyclic functional side-group on the β -lactone and the stereoelectronic tuning arising from the phenolate ligand *ortho*-substituents on the yttrium coordination sphere, is evidenced in the control of the stereoselectivity of the ROP through the implementation – or not – of NCIs. These achiral rare earth catalyst systems thus afforded a remarkable stereocontrol in the ROP of original functional *racemic* β -lactones, among which the first sulphur-substituted PHAs, ultimately providing PHAs with tunable thermal properties, and further highlighting their valuable potential.

Conflicts of interest

There are no conflicts to declare.

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