Polyesters

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Variably Isotactic Poly(hydroxybutyrate) from Racemic β-Butyrolactone: Microstructure Control by Achiral Chromium(III) Salophen Complexes**

Manuela Zintl, Ferenc Molnar, Tobias Urban, Volker Bernhart, Peter Preishuber-Pflügl, and Bernhard Rieger**

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

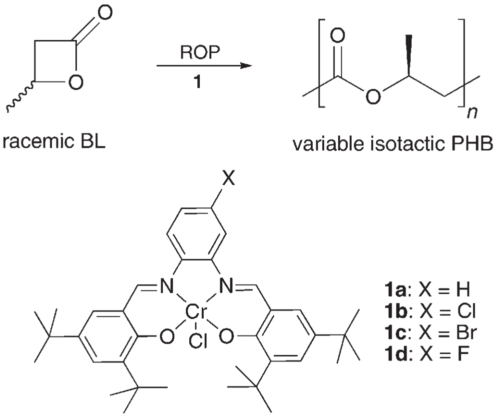
Produced by bacteria and microorganisms, the highly isotactic poly(hydroxybutyrate) (PHB) is an interesting biodegradable polymeric material. Owing to its comparable mechanical properties, it is an attractive alternative to polyolefins, especially isotactic polypropylene (*i*-PP).[1] However, as long as PHB fabrication through biotechnological routes remains cost intensive, polyolefins win the contest.

Therefore, efficient chemical synthesis pathways for this natural polyester motif are of significant importance. There are two major strategies, which are based on the cheap industrial monomers propylene oxide (PO) and carbon monoxide (CO). In addition to the newly discovered direct alternating copolymerization of epoxides and CO,[2] the two-step procedure of combining PO carbonylation to give β-butyrolactone (BL)[3] with subsequent ring-opening polymerization (ROP) is promising.

In the ROP of racemic BL, aluminoxane (AlR_3/H_2O) catalysts generate mixtures of different tacticities, which can be isolated by fractionation. Medium, in some cases higher molecular weights and broad polydispersity indexes (PDIs) are reported, however, reaction times of several days are required.[4] A sometimes higher stereoregularity can be achieved with chiral aluminum(III) salen or -porphyrin complexes.[5] Zinc alkoxides (e.g. from $ZnEt_2/H_2O$) are more active, but only amorphous polymers are produced.[6] To circumvent this disadvantage chiral ligands have been introduced, however, although the isotactic polymer was formed the activity was reduced. Syndiotactic PHB of various molecular weights is generated with tin(II,IV)-based catalysts.[7] Recently, the group of Carpentier showed that a syndiotactic PHB (with interesting properties) can even be obtained by yttrium(III)-catalyzed ROP.[8]

Perfectly isotactic PHB (bacterial (*R*)-PHB) is brittle and stiff with a decomposition temperature slightly above the melting transition.[1] Isotacticities ranging from 60 to 80% are desired to generate properties comprising those of elastomeric to plastomeric materials.[9] A major second requirement to establish a new family of high-performance polymers is a molecular weight exceeding 2×10^5, or even more desirable, $5\times10^5\,\mathrm{g\,mol^{-1}}$.[10]

Herein we report chromium(III) salophen[11] complexes for the stereoselective ROP of racemic β-butyrolactone (Scheme 1). Surprisingly, for the first time, these achiral structures, merge the three important features of high activity and high molecular weight with control of the polymer microstructure, affording the desired variably isotactic PHB. Furthermore, all three factors can be influenced by catalyst design (**1b–d**), opening the way to a broad family of high molecular weight PHB materials.



Scheme 1. Chromium(III) salophen complexes.[14] In place of the phenyl bridge, **2a** and **2b** have (1*S*,2*S*)-cyclohexyl and (1*S*,2*S*)-diphenylethyl bridges, respectively.

Catalyst **1a** was found, depending on the reaction time (up to 20 h), to afford complete conversion of the monomer. The polymeric material produced is a semicrystalline powder with a molecular weight of $190\,000\,\mathrm{g\,mol^{-1}}$ (Table 1). The dyad (*m*, *r*) signals (quaternary C atom: $\delta = 169$ ppm) in the ^{13}C NMR experiment are used to determine the stereoregularity,[15]

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[*] Dr. F. Molnar, Dr. V. Bernhart, Dr. P. Preishuber-Pflügl
BASF Aktiengesellschaft, 67056 Ludwigshafen (Germany)
E-mail: peter.preishuber-pfluegl@basf.com
Prof. Dr. B. Rieger
WACKER-chair of Macromolecular Chemistry, TU Munich
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13562
E-mail: Rieger@mytum.de
Dipl.-Chem. M. Zintl, Dr. T. Urban
University of Ulm
Institute of Materials and Catalysis

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Table 1: ROP of racemic BL.[a]

Catalyst	t [h]	Conv. [%][b]	Isotacticity [%]	T_m [°C]	M_w [kg mol^{-1}]/ PDI[c]
1a	5	36	64	121, 149	190/8.5
1b	5	81	63	120, 143	780/9.6
1d	5	79	66	116, 142	250/5.2
2a, **b**[d]	5	2–3	atactic	–	–
2a, **b**[d]	20	16,19	atactic	–	>10

[a] Polymerizations were performed in pure monomer, $T = 100$°C, catalyst/BL = 1:1000. [b] Determined by ^{1}H NMR spectroscopy. [c] The broad PDI results from, among others, the high viscosity which hinders a uniform polymer formation in bulk polymerization.[16] [d] **2a**: [(1*S*,2*S*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamino]chromium (III) chloride; **2b**: [(1*S*,2*S*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-diphenylethylene-1,2-diamino]chromium (III) chloride.

indicating the formation of isotactic PHB in the range of $60 \leq m \leq 70\,\%$ (Figure 1). As a result of their lower isotacticity the melting transition temperatures of these polymers are lower than that of bacterial PHB, which enables the new polymers to be handled in molten form without decomposition.

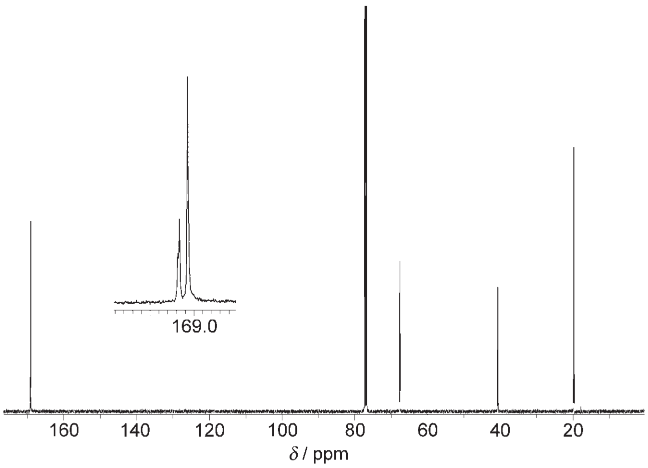

Figure 1. ^{13}C NMR spectrum of the obtained variably isotactic polymer.

First indications that a binuclear reaction mechanism was the origin of the enantioselectivity came from DFT investigations. They show that a nucleophilic attack of the coordinated BL by Cl$^-$ ions gives a chromium carboxylate species (**A**). Compound **A** is able to ring-open further coordinated BL for PHB generation, whereas the polymerization of free lactone is slightly endothermic and has a high activation barrier (ca. 70 kJ mol^{-1}).

The isospecificity observed for the ROP reaction cannot result from enantiofaciale BL discrimination on a single {Cr^{III}(salophen)} center, owing to the achiral nature of this center. DFT calculations, however, support the formation of binuclear structures, which form a tight chiral cage by entrapping the stereogenic center of the last inserted monomer unit within the sandwich structure (Figure 2 and Supporting Information).[17] Interaction of the phenyl bridge and the *tert*-butyl groups of two chromium(III) complexes with the growing chain opens a chiral reaction channel that preferentially accommodates one BL enantiomer. In addition, the calculations show that the sandwich structure proposed is not tight enough to afford completely isotactic polymer.

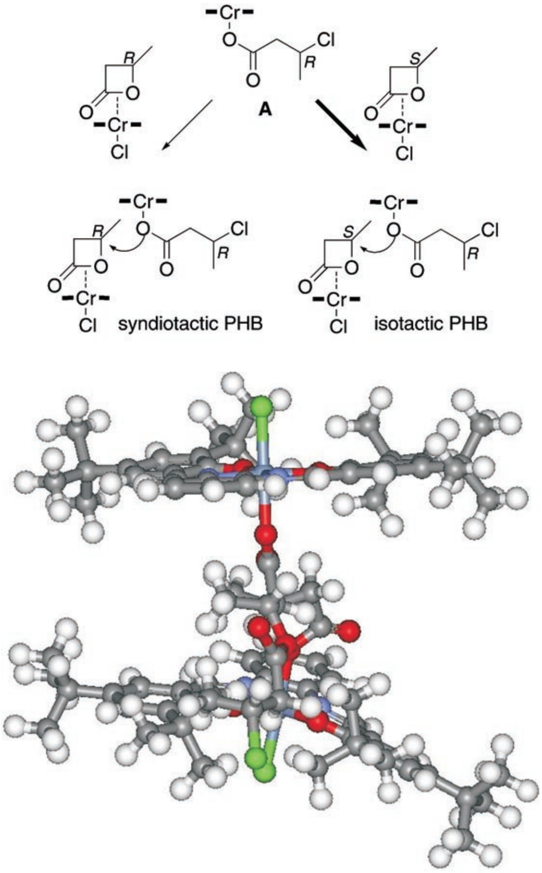

Figure 2. Results of DFT calculations: top: proposed mechanism, bottom: PHB formation in a sandwich-like structure of two chromium(III) salophen units; blue Cr, red O, green Cl. Ring-opening of BL through the carboxylate species results in an inversion of configuration.

These first results encouraged us to take a closer look at ROP reactions catalyzed by differently substituted chromium(III) salophen complexes to see if manipulation of the PHB microstructure through catalyst design is possible. Exchange of the phenyl unit (**1a**) by a chiral (1*S*,2*S*)-cyclohexyl (**2a**) or (1*S*,2*S*)-diphenylethyl bridge (**2b**), often used for aluminum(III)-based ROP catalysts,[13] gave even after a day only traces of polymers. The introduction of halogen atoms to the original phenyl bridge (Scheme 1, **1b**–**d**), however, resulted in surprising improvements. Catalyst **1d**, characterized by a 4-fluorophenyl group proved to be two times more active than **1a** and gives a molecular weight of about 250 000 g mol^{-1}. The 4-bromo (**1c**) and 4-chloro (**1b**) substituted derivatives show the same high activity, but also result in significantly improved molecular weights of up to 780 000 g mol^{-1} while the tacticities stay almost constant (Table 1). To date we have no explanation for the substitution effects. DFT calculations, however, point towards a combination of steric and electronic effects between the two salophen units and the growing polymer chain.

The achiral chromium(III) salophen complexes investigated for the ROP of β-butyrolactone combine high activity with high molecular weight and interesting tacticities of the PHB products. In addition, the catalyst performance can be influenced by varying the aryl substituents on the salophen framework, thus allowing improved control of the polymer properties by catalyst design. Future work will concentrate on improving the molecular weight distribution and increasing the catalyst activity, a prerequisite for industrial applications.

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