Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 9311–9317 **9311**
DOI: 10.1021/ma101407r

Factors Influencing the Ring-Opening Polymerization of Racemic β-Butyrolactone Using Cr^{III}(salphen)

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Received June 30, 2010; Revised Manuscript Received September 17, 2010

ABSTRACT: The recently discovered ring-opening polymerization (ROP) of β-butyrolactone (β-BL) using Cr^{III}(salphen) as catalyst converts racemic β-BL to isotactic enriched poly(hydroxybutyrate) (PHB). These achiral complexes arrange themselves in a dimeric sandwich-like structure entrapping the growing polymer chain and the monomer. The polymerization mechanism discussed based on previous DFT calculations is supported by kinetic studies in here. Furthermore, the influence of different substitution patterns in salphen complexes on polymerization of β-BL was investigated. In addition, effects of different polymerization starters and additives on the broad molecular weight distribution of PHB have been investigated, which show the limitations of this catalysis.

Introduction

Poly(hydroxybutyrate) (PHB) is a naturally occurring aliphatic polyester, that is produced by a variety of bacteria and microorganisms as an internal energy and carbon reserve and thus features biodegradation and biocompatibility. Furthermore, the mechanical properties of these biopolymers are similar to those of standard commodity polymers, which opens the chance for many applications not only as a niche product in the medicine sector (e.g., as artificial tissues or drug delivery systems) but also as a competitor to standard oil-based plastic materials. In particular, the packaging industry and agriculture are proposed for this increasingly important biopolymer.[1,2]

The natural PHB is a completely isotactic (R) polyester of high crystallinity that decomposes slightly above its melting transition, causing difficulties in industrial manufacturing. Hence, formation of high-molecular-weight aliphatic polyesters with reduced crystallinity would be favorable. Up to now, PHB is produced by biotechnological methods. The only possibility for the desired lower melting transition so far was achieved by changing the nutrient media of the applied bacteria, affording copolymers like BIOPOL. However, the nonhomogeneous polymer composition unfavorably influences the mechanical properties of the material. Instead, lowering the melting point by reduction of the tacticity seams to be a more promising way. Moreover, the bioengineering route to PHB is expensive compared with the chemical synthesis of commodity polymers. To compete with them in regards to the price, a synthetic pathway to poly(hydroxybutyrate) of controlled stereoregularity from commercial educts is required.

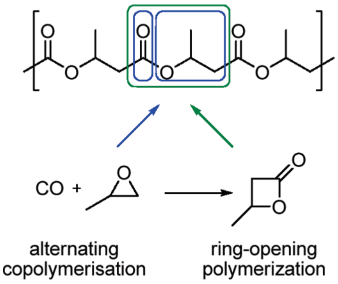
From a retrosynthetical point of view, racemic propylene oxide (PO) and carbon monoxide (CO) are attractive building blocks for PHB formation (Scheme 1). Besides the direct alternating copolymerization, there is also a ring-expansion reaction of the epoxide with CO yielding β-butyrolactone (β-BL), which is a suitable monomer for ring-opening polymerization (ROP).

The recently discovered direct alternating copolymerization of PO and CO combines the ring-opening reaction of the cyclic ether and insertion of CO.[3] This cobalt-catalyzed copolymerization is, so far, not developed for the stereoselective synthesis of high-molecular-weight PHB out of racemic PO. For the introduction of stereoinformation, enantiopure epoxide is necessary,[4] which results in increasing production complexity and costs, and the realizable molecular weight is much too low for industrial purposes.[4−6] Another way to get control over stereochemistry is the application of chiral carbonylation catalysts, which convert racemic PO to enantiomerically enriched β-BL, followed by its polymerization with retention of the stereogenic center. However, the activities of such catalysts are too low, and the enantiomeric excess (ee) reached so far is <33%.[7,8] Therefore, attention was turned toward the polymerization of racemic β-BL, which has gained much research interest during the past decades, resulting in a development of several types of ROP-active catalysts.

These systems differ in activity and generated microstructure of the polymer. Completely isotactic PHB is a brittle and stiff material comparable to poly(ethylene therephtalate) if no additives are used. Atactic PHB is oily and of no use in common plastic technology. However, Doi and coworkers found out that an isotacticity of $0.65 < P_m < 0.80$ and a molecular weight of 200000 g/mol afford a thermoplastic material with mechanical properties comparable to those of isotactic poly(propylene).[9]

Stereoinformation can be delivered by aluminoxane catalysts, but the produced PHB is not uniform with respect to stereoregularity. After fractionation, isotactic polymers with broad PDI can be isolated.[10,11] Isotactic polyester can be synthesized by

Scheme 1. Possible Routes Towards PHB



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aluminum(III)-based porphyrins or salens. However, their activity is low, and reaction times of several days are required.[12] A more active catalyst group is based on $ZnEt_2/H_2O$, although only atactic material is obtained in this case. Tactic microstructures can be achieved by the addition of a chiral diols, but it slows down the reaction significantly.[13,14] Syndiotactic polymers can be synthesized by applying either tin-based or rare-earth-metal-based catalyst.[15−17] Carpentier et al. reported on a variety of active yttrium compounds giving high-molecular-weight polymer of syndiotacticities up to 98%;[18,19] however, catalysts that convert racemic β-BL to middle-ranged isotactic polymers are rare. Gauvin reported on silica-supported rare earth metal catalysts that afford polymers up to 12 000 g/mol (M_n) with an isotacticity of 0.85 (P_m), but long reaction times of 16 h are necessary.[20]

A new group of active catalysts that allow us to polymerize racemic β-BL with molecular weights up to 800 000 g/mol (M_w) are Cr^{III}(salphen)s. In addition, these achiral catalysts can even control the microstructure of the produced polymer.[21] The initiation of polymerization process occurs via alkyl-clevage of the β-lactone after nucleophilic attack of a chlorine anion on the tertiary carbon atom of an activated β-BL. The resulting reactive carboxylic end group coordinated to Cr^{III}(salphen) complex is now capable of opening further lactones and continuing the polymerization, in which two salphen complexes arrange themselves in a cage-like dimeric structure affording predominantly isotactic PHB in a range of $0.60 < P_m < 0.70$. These catalytic systems therefore combine high catalytic activity and high molecular weight of produced polymers with the desired stereocontrol under ambient reaction conditions.[21]

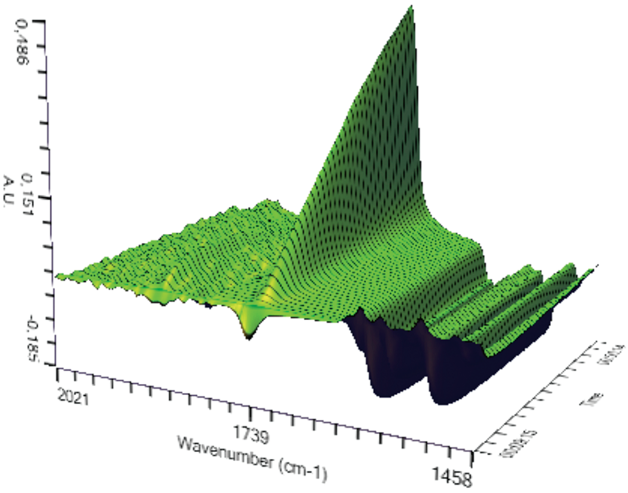


Figure 1. ATR-IR stack plot: polymerization growing polymer signal at 1744 cm^{-1}.

Herein we report on a study of the Cr^{III}(salphen)s catalyzed ROP of β-butyrolactone including the investigation of electronic and steric effects within the ligand as well as of the influence of different reaction components that control the polymerization.

Results and Discussion

Various salphen ligands were synthesized by condensation of differently substituted salicylaldehydes with various commercially available *o*-phenylenediamines. This ligand library features novel salphen derivatives with modified sterical and electronical demand. The subsequent metalation using $CrCl_2$ and oxidation on air affords the respective complexes in almost quantitative yield.

In the first instance, kinetic studies using complex **1** as a catalyst of known activity were performed to verify the reaction mechanism resulting from DFT calculations.[21] Online ATR-IR spectroscopy has been shown to be a useful tool to get a direct insight into a reaction. Using this technique, the polymerization can easily be followed by a linear growing polymer signal at 1744 cm^{-1} (Figure 1) after a short latency period due to initiation mechanism, which is further discussed later.

This result gave us the occasion to have a closer look into the kinetics of the reaction. ^1H NMR monitoring was chosen for quantitative evaluation of kinetics determined by IR. Jacobsen et al. could prove that two Cr^{III}(salen) complexes were involved in a catalytic cycle of an asymmetric epoxide ring-opening by varying the catalyst concentration and measuring the reaction rate.[24,25] Similarly, the ratio of catalyst **1** to β-BL was varied in our experiments from 1:500 to 1:10 000, giving the linear consumption of monomer at the initial period of the reaction (pseudo-zero-order reaction conditions) (Figure 2).

These data were used for determination of the catalyst reaction order. The resulting value of 1.3 indicates that on average more

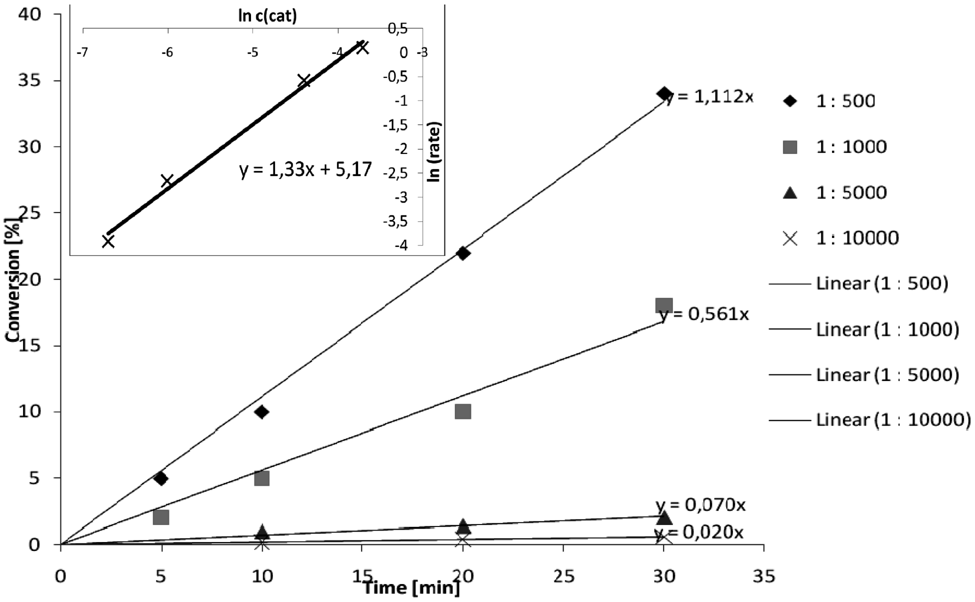


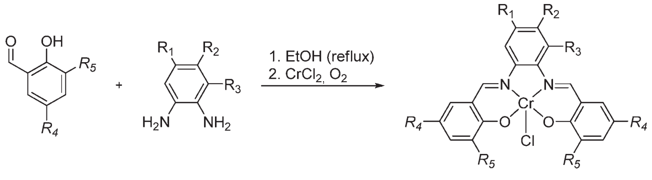
Figure 2. Time-dependent conversion, followed by ^1H NMR and IR after latency period, catalyst **1** in the given ratios, T = 100 °C; determination of the reaction order.

than one catalyst molecule is involved in the transition state (TS). This finding fits our previously published results of DFT calculations affording energetically different possible reaction pathways for the growing chain (Scheme 3).[21] In a dual-site catalysis, two Lewis acid molecules are involved. The first is bound to the polymer chain and prevents backbiting, whereas the second one activates the monomer. They arrange in a sandwich-like structure, giving a chiral cage (Figure 3). This intermediate cage transcribes the chirality to the monomer, where now in an exothermic reaction ($\Delta H = -33$ kJ/mol, $E_a = 45$ kJ/mol) one enantiomer is preferred, affording an isotactic section in the chain.[21] Such reaction mechanism has already been reported for copolymerization reactions of CO_2 and various epoxides but not yet for the ROP of lactones.[26,27] Our DFT calculations have also shown further reaction pathways. The growing chain bound to Cr^{III}(salphen) can react in a slightly endothermic reaction ($\Delta H = 10$ kJ/mol, $E_a = 74$ kJ/mol) with a noncoordinated β-BL (reaction with uncoordinated lactone). This reaction involves the cleavage of the growing chain from the catalyst and is thus one reason for the observed low reaction control that is further discussed later. Additionally, the reaction of the resulting uncoordinated chain with an activated monomer was investigated, and an exothermic reaction of moderately low activation energy ($\Delta H = -97$ kJ/mol, $E_a = 33$ kJ/mol) was found, which again leads to a growing chain coordinated to one catalyst. In the latter two pathways, only one catalyst molecule participates in the TS. Because of the achiral structure of these complexes, no stereoinformation is transferred, which results in an atactic domain. All discussed reactions show moderate activation energies and reaction enthalpies. (More detailed information on performed DFT calculations can be found in the supporting information of ref 21.) The interplay of all of these is reflected in the observed fractional reaction order of the catalyst and explains the obtained slightly isotactic enriched microstructure of resulting PHB.

The reaction mechanism offers a possibility to get influence on the microstructure of the polymer. Fitting the chiral cage by peripheral substitution in salphen ligand could increase the thermodynamic differentiation of the two pathways and influence the tacticity.

Investigation of the Electronic Demand. Scheme 2 gives a sketch with applied variation of the substitution pattern in salphens. By introduction of substituents in R_3, R_2 and R_2, R_1 positions, different novel and literature known ligands and complexes have been prepared (Table 1). The introduction of a methyl group to the R_2 position (catalyst **2**) gives only a slight increase in productivity but a decrease in molecular weight and isotacticity of obtained PHB, as compared with **1**. However, the methyl group in the R_3 position (**3**) gives a nearly inactive complex, producing polymer of low M_w and atactic microstructure. Obviously, electronic effects play a crucial role in polymerization activity because the position of a weak donor like CH_3 shows such a high impact. If an electron-donating group (t-Bu) is introduced to the catalyst (**4**) in the R_2 site, then, again, low activity is observed. Obviously an increasing electron density on the Lewis acid center weakens bonding to the monomer and the growing chain and thus explains the poor polymerization results. Indeed, electron-density-withdrawing

Scheme 2. Differently Substituted Cr^{III}(salphen)s for the ROP of β-BL



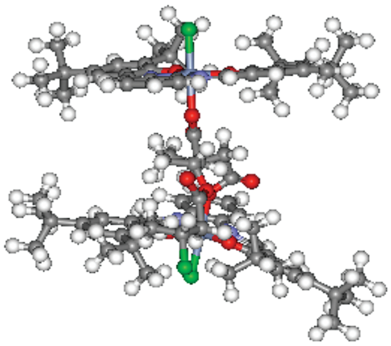


Figure 3. DFT calculation: PHB formation in a cage of the dimeric Cr^{III}(salphen) sandwich-like structure (reproduced with permission of *Angew Chem.* from Reference 21).

Scheme 3. Energetically Different Pathways Affording Variable Polymer Microstructures

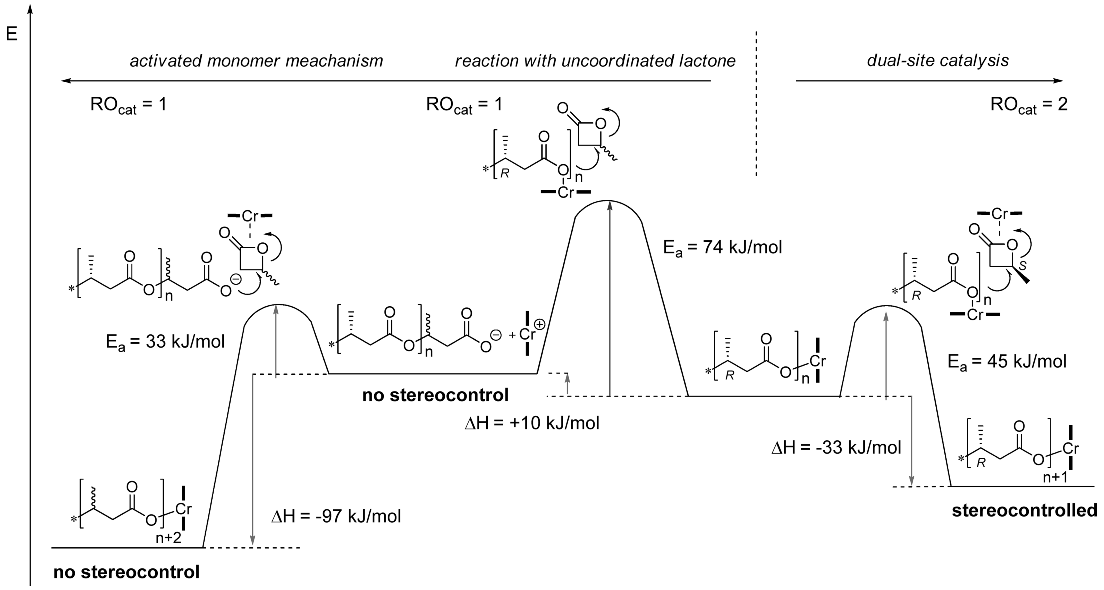


Table 1. Polymerization Results of Different Substituted $\mathrm{Cr^{III}}$(salphen)s, $T = 100°\mathrm{C}$, 5 h, cat/β-BL = 1/1000

catalyst	R_1	R_2	R_3	R_4	R_5	Y [%][a]	M_w [10^3 g/mol][b]	PDI	P_m[c]
1	H	H	H	t-Bu	t-Bu	36	186	8.0	0.64
2	H	Me	H	t-Bu	t-Bu	48	120	8.2	0.60
3	H	H	Me	t-Bu	t-Bu	8	5.1	1.6	0.50
4	H	t-Bu	H	t-Bu	t-Bu	20	6.7	1.3	0.50
5	H	F	H	t-Bu	t-Bu	79	254	5.2	0.66
6	H	Cl	H	t-Bu	t-Bu	81	780	8.5	0.65
7	H	Br	H	t-Bu	t-Bu	80	650	6.7	0.67
8	Cl	Cl	H	t-Bu	t-Bu	63	217	6.6	0.60
9	H	CF_3	H	t-Bu	t-Bu	40	53	4.3	0.52
10	H	CN	H	t-Bu	t-Bu	6	5.3	2.2	0.50
11	H	H	H	t-Bu	H	5	5.0	1.8	0.50
12	H	H	H	H	t-Bu	7	6.1	1.9	0.51
13	H	Cl	H	t-Bu	H	13	6.7	2.1	0.53
14	H	Cl	H	H	t-Bu	15	5.8	1.9	0.51

[a] Y conversion, determined by ^{1}H NMR spectroscopy from reaction mixture. [b] Determined by GPC against poly(styrene) standards. [c] Determined by ^{13}C NMR spectroscopy; P_m gives the probability of meso-dyade linkages between monomer units according to literature.[22,23]

halogens in R_1 and R_2 positions increase the activity considerably. Substitution by F (**5**), Cl (**6**), and Br (**7**) give catalysts of high productivity. These complexes convert racemic β-BL to polymers with an isotacticity of ~0.65 (P_m) and molecular weights ranging from 250 000 to 800 000 g/mol. However, too strong acceptors like CF_3 (**9**) and CN (**10**) decrease activity again, which can be explained by enhanced affinity of the growing polymer chain to one catalyst center, hindering the transfer to the activated monomer at the second complex. (See Table 1.) The introduction of further halogens by substitution of the t-Bu groups in the R_4 and R_5 positions led to very poor soluble ligands, which could not even be converted to the corresponding complexes. Surprisingly, partial exchange of the t-Bu groups in R_5 (**11**) or R_4 (**12**) positions of salicylaldehyde moieties by hydrogen atoms leads again to atactic oligomers (M_w < 10 000 g/mol). This might be caused by poorer solubility due to increased aggregation of such complexes in β-BL, resulting in an effective blockage of the active centers and clarifying the importance of the t-Bu groups in both the R_4 and R_5 positions. Even introduction of chlorine to the backbone cannot overcome this effect, which was verified by the use of monochlorinated salphens **13** and **14**.

Investigation of the Initiation Step. DFT calculations indicate the initial ring-opening of β-BL by a chloride in the presence of a suitable Lewis acid, which remains covalently bound to the growing chain (Scheme 4).[21] Mass spectrometry would be an appropriate tool, providing a proof for the presence of chlorine as a polymer chain end group. However, no suitable conditions for the analysis of PHBs by either MALDI or ESI-MS could be found. EDX analysis indicates the presence of Cl and Cr atoms in raw polymer in nearly equimolar ratio. To get a hint for the binding character of chlorine in the polymer sample, it was exposed to ion-exchanger for several days. EDX measurements show that in so-treated polymer no Cr can be found, although the amount of Cl stays the same as that before the treatment, thus indicating that chlorine is covalently bound to the polymer. (See the Supporting Information.)

Furthermore, the importance of the chloride for the initiation could easily be proved. When $AgSbF_6$ was used to detach chloride from **1**, the resulting cationic chromium complex (**1b**) was no longer active in the ROP of β-BL. Elemental analysis of this complex proved that all chloride was replaced by SbF_6^-. After the addition of small amounts of PPNCl to **1b**, the catalytic activity could be partially recovered. By adding 0.2 to 1.0 equiv of PPNCl to the original complex **1**, an increase in activity in terms of conversion was observed, although the molecular weight of the products breaks down dramatically, and the resulting oligomers show an atactic microstructure. Free chlorines compete with the growing chains for coordination sites on the catalyst, which lowers the average number of coordinated chains on each catalyst molecule. Therefore, the already low probability for such dual site catalysis decreases to zero, which explains the obtained atactic microstructure. In addition, noncoordinated chain ends suffer from backbiting reactions, affording oligomeric macrocycles,[28] which were the only detectable products using MALDI. The overall higher activity can be explained, on one hand, by the ability of free chlorine to open β-BL in the presence of a suitable Lewis acid[29] and, on the other hand, by decreased diffusion limitations due to the obtained lower molecular weight. Moreover, substitution of the Cl^- in **1** by known initiator $OAc^{-30,31}$ using silver acetate giving complex **1a** only marginally affects the polymerization. Thus, chlorine is nucleophilic enough to start the polymerization similarly to the acetate (Table 2).

Scheme 4. Initiation of the ROP using $\mathrm{Cr^{III}}$(salphen)

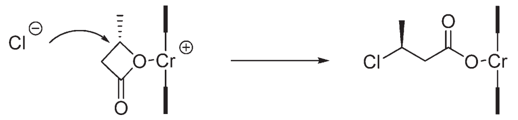


Table 2. Influence of Initiator; T = 100 °C, t = 5h

cat	PPNCl equiv	Y [%]	P_m	M_W [10^3 g/mol]	PDI
1	0	36	0.64	186	8.0
1a	0	34	0.61	213	9.1
1b	0	5	0.50	2.0	1.6
1b	0,2	20	0.60	50	4.5
1	0,2	40	0.58	12	3.7
1	0,5	44	0.50	3.5	1.7
1	1	58	0.50	4.7	2.0

Factors Influencing the Polymer Characteristics. The molecular weight of the produced polymers is not only dependent on the structure and composition of the catalytic system but also on the purity of the lactone. According to GPC data, water in ratio 1:1000 to lactone provides oligomers up to 10 000 g/mol (M_w), which means that low-molecular-weight fraction in the polymerization can also result from residual water in the reaction mixture. Furthermore, water in β-BL also reacts to form 3-hydroxybutyric acid (3-HA), which is typically present in commercial β-BL in different amounts depending on the batch. By the addition of small amounts of commercially available 3-HA to a standard polymerization of specially purified β-BL and catalyst **1**, the overall conversion increases, but molecular weights of resulting PHB decrease significantly (Table 3), so just 0.1 mol % of 3-HA in lactone leads to a decrease in M_w by > 50%. These experiments prove that this catalytic reaction is highly sensitive to 3-HA resulting from residual water. Free hydroxyl group of 3-HA can open activated β-BL, affording the hydroxyl-terminated atactic oligomers, which can cleave any ester group of the polymer by transesterification. This leads to a decrease in the molecular weight of resulting PHB and is also in agreement with the observation that prolonged reaction times cause a decrease in the polymer molecular weight. (See Figure 4.) The interplay of these two parallel processes, namely, the polymerization and transesterification caused by traces of 3-HA, is responsible for the observed trends.

The typical synthetic procedure for the $\mathrm{Cr^{III}}$(salphen)(Cl) catalyst includes a workup in aqueous media. Therefore, water can be present as a sixth ligand in these octahedral

Table 3. Influence of 3-Hydroxybutyric Acid on Molecular Weight (M_w), cat = 1, T = 100 °C, reaction time = 5 h

3-HA [mol %]	Y [%]	M_n [10^3 g/mol]	M_w [10^3 g/mol]	PD
0	36	23.3	186.0	8.0
0.10	85	21.0	62.0	3.0
0.22	91	15.7	51.0	3.2
0.44	88	11.9	35.0	2.9
0.66	90	15.3	49.0	3.2
0.88	85	16.0	48.0	3.0
1.80	80	9.3	29.0	3.1
2.20	83	6.2	22.0	3.5
4.40	76	4.0	14.0	3.5

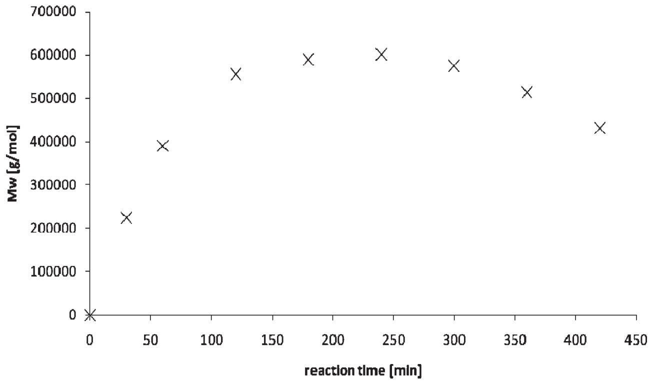


Figure 4. Influence of reaction time on molecular weight (M_w), cat = **1**.

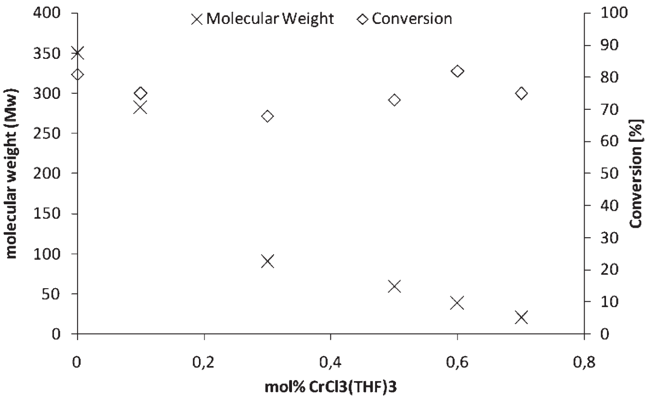


Figure 5. Influence of $CrCl_3(THF)_3$ on molecular weight (M_w) and conversion, standard reaction conditions using catalyst **6**.

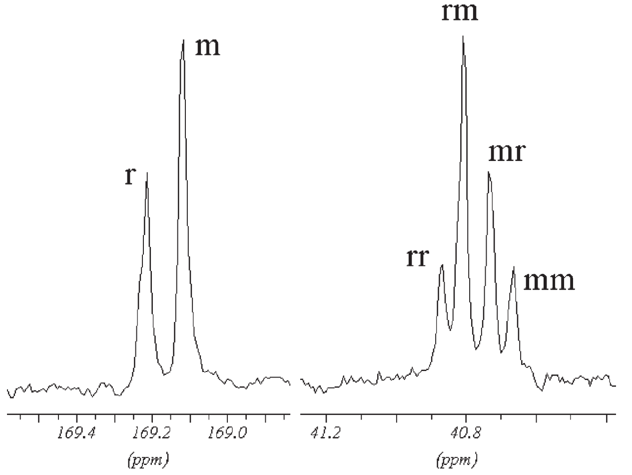


Figure 6. ^{13}C NMR: carbonyl and methylene region of isotactic enriched polymer resulting from bulk polymerization.

Cr^{III}-complexes depending on the conditions of the drying protocol, which was also indicated by poor reproducibility of the elemental analysis. The catalyst synthesis can also be performed via a water-free procedure using $CrCl_3(THF)_3$ and the potassium salt of the salphen ligand in equimolar ratio according to literature,[32] although such complexation is much slower compared with the reaction with $CrCl_2$. Surprisingly, thus-prepared complexes generate only oily materials unless they were exposed to air during workup. We explain these results by the presence of the air- and moisture-sensitive impurities in the catalyst, such as excessive $CrCl_3(THF)_3$, for example, which disturb the polymerization. Indeed, the addition of small amounts of $CrCl_3(THF)_3$ to the polymerization with active catalysts has shown a strong decrease in molecular weight of resulting PHBs without affecting the conversion (Figure 5). Most probably, $CrCl_3(THF)_3$ cleaves the bonding of the growing polymer chain to the catalyst decreasing M_w and plays a role as the Cl^- source for the regenerated complex cation to initiate a new chain.

As an alternative to the oxidation by air in the typical procedure, Cr^{III}(salphen) complexes can also be prepared in the presence of pestled Na_2O_2. In the standard polymerization reaction with thus synthesized complexes **1** and **6**, the achieved molecular weights differ marginally from those obtained with air-oxidized complexes, but the conversion increased from 36 to 50% and from 80 to 100%, respectively.

In addition to the observations described above, the effect of the solvent on the polymerization should be noticed. The standard polymerization with Cr^{III}(salphen) complexes is carried out in neat β-BL and thus suffers from many problems. The viscosity of the media rises with increasing conversion of the monomer. Even solid materials can be obtained depending on the amount of reacted monomer and the range of the molecular weight of the polymer. Inhomogeneous polymerization conditions and, as a result, broadened molecular weight distributions (PD) are the disadvantages of such bulk polymerization. Therefore, alternative polymerizations in solution have been performed. Because of solubility reasons and because of suitable boiling point, chlorobenzene and toluene have been chosen as proper solvents for the polymerization at 100 °C. Depending on the amount, the overall viscosity of the polymerization media could be appropriately decreased. Therefore, 50 vol % of solvent allowed us to avoid the otherwise imminent solidification of the reaction mixture. Under such conditions, the polymerization is more homogeneous, and the molecular weight distributions of resulting PHBs are decreased. Whereas the ratio of catalyst to monomer was kept constant in such polymerizations, dilution with solvent slows down the reaction. If complex **7** or another halogenated catalyst is used, then 60% conversion is still obtained in 5 h of reaction time with molecular weights of up to 500 000 g/mol (50 vol % chlorobenzene). The use of either chlorobenzene or toluene does not cause significant differences.

However, analysis of the polymer generated with catalysts **6** and **7** in solution shows a change of microstructure from isotactic enriched to slightly syndiotactic of the same range ($0.60 < P_r < 0.70$) as the one from the polymerization in neat lactone (Figures 6 and 7). DSC measurements show no melting transitions, which can be explained by poorer crystallization of syndiotactic domains compared with isotactic domains.

It is remarkable that both **6** and **7** are asymmetrically substituted in the backbone. In contrast, PHBs obtained in solution with symmetrically substituted catalysts **1** and **8**

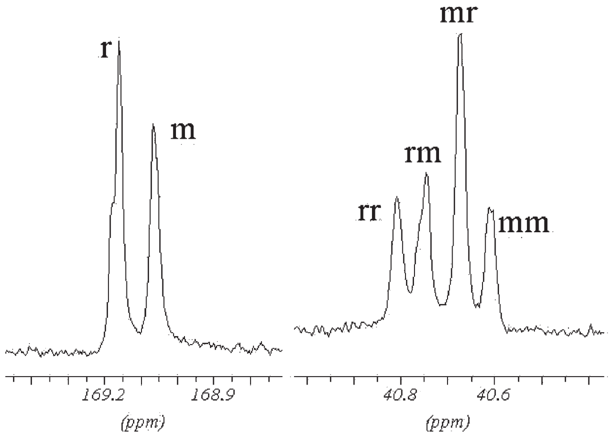


Figure 7. ^{13}C NMR: carbonyl and methylene region of syndiotactic enriched polymer obtained from solvent polymerization.

Table 4. Results of Polymerization in Chlorobenzene at T = 100 °C

catalyst	vol % solvent	conversion [%]	tacticity	M_w [10^3 g/mol]	PDI
1	50	20	iso	120	6.2
6	60	59	syndio	340	4.7
6	50	60	syndio	530	7.1
7	60	50	syndio	440	5.8
8	60	36	iso	200	7.0

retain the partial isotacticity, as when they were prepared in bulk (Table 4). Therefore, the symmetry of the phenylene ring in the backbone of the salphen complex has influence on the generated microstructure in solution but not in bulk. This finding can be explained only by interactions of the solvent molecules with the TS of the reaction, but too many parameters influence both operating reaction mechanisms for a more detailed investigation.

Conclusions

Cr^{III}(salphen) complexes are able to perform the ROP of racemic β-BL with increased isotacticity of resulting polymer. These achiral catalysts arrange into a dimeric cage-like chiral structure during the polymerization, thus inducing the partial stereoregularity to PHB. The herein presented kinetics supports such dual-site catalysis from previously reported DFT calculations. In general, it was shown that both steric and electronic influences of the substituents play a crucial role in the differences in activity of salphen catalysts and properties of resulting PHBs. The introduction of electron-density-withdrawing halogens enhances catalytic activity up to a certain point without affecting stereoselectivity, compared with the unsubstituted catalyst, and it also increases molecular weights of PHBs significantly, but stronger withdrawing groups lead to an increased binding of the catalyst to the growing polymer chain, which slows down the reaction. In addition, t-Bu in R_4 and R_5 groups is necessary in both positions to avoid the problems of solubility and aggregation. However, this polymerization suffers from many limitations. A strong influence of water, 3-hydroxybutyric acid, and of residual precursor $CrCl_3(THF)_3$ on the molecular weight was found. The described observations demonstrate all of the sensitivity of the herein studied catalytic system.

Experimental Section

Commercially available chemicals were used without additional purification, unless mentioned. THF was distilled over $LiAlH_4$. β-Butyrolactone was rectified over CaH_2 using a 1.8 m turning band column prior to use. Synthesis and polymerization reactions were performed by standard Schlenk techniques under argon.

Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AMX500 or Bruker ARX300. Chemical shifts δ are given in ppm in reference to ^{1}H NMR and ^{13}C NMR signals of the deuterated solvents. Molecular weight data were obtained from gel permeation chromatography (GPC) with $CHCl_3$ or $CHCl_3$/0.1% $(Bu)_4NBF_4$ as solvent in reference to polystyrene. Thermal transitions of the polymer samples were monitored using a Perkin-Elmer DSC-7 with scan rates of 10 K/min. IR autoclave investigations were carried out in a MultiMax ReactIR apparatus from Mettler Toledo.

Ligands and complexes were synthesized according to literature procedures[32] or as described in the Supporting Information.

General Synthesis Procedure. The phenylenediamine derivative and excess of the related salicylaldehyde (2.2 times) were refluxed in EtOH p.A. for several hours. The obtained precipitate was filtered off, washed with EtOH, and dried under high vacuum. If necessary, it was additionally recrystallized (from EtOH p.A.).

The ligand was transferred to a Schlenk flask provided with 1.3 equiv of $CrCl_2$ under argon. The mixture was dissolved in absolute THF and stirred for several hours under an argon atmosphere. Then, the solution was allowed to stir under air overnight. The organic phase was washed two times with saturated Bu_4NCl solution and dried over Na_2SO_4. After filtration, the solvent was evaporated to give a reddish brown powder.

General Polymerization Procedure (Standard Schlenk). The appropriate amount of the catalyst was introduced to the Schlenk tube under argon, followed by the addition of β-butyrolactone. The polymerization was performed at 100 °C. After the desired polymerization time, the reaction was allowed to cool to room temperature. The NMR sample in $CDCl_3$ was prepared to obtain the degree of conversion. Then, the polymer was precipitated by Et_2O/n-hexane (50/150 mL per 1 mL of reaction mixture). If the polymer solution was too viscous or solid, then CH_2Cl_2 was used to dissolve the polymer before it was worked up. The liquid was decanted, and the polymer was washed again with Et_2O/n-hexane and dried until constant weight.

Theoretical Method. The overall polymerization reaction was conceptually split into several steps. For each of the steps, the corresponding reaction mechanism was investigated by locating the TS and the associated reactants and products. The nature of all TSs was verified (only one negative eigenvalue of the Hessian). We identified reactants and products by inducing small distortions in the TS structure along the eigenvector associated with the negative eigenvalue. Distortions with positive and negative amplitude lead to reactants and products after subsequent geometry optimization. All calculations were performed with the quantum chemistry package TURBOMOLE.[33] DFT methodology was used at the B-P86/SV(P)[34−36] level of theory to locate all stationary points. Single-point energy calculations were carried out using the TZVP[37] basis set. Geometries were optimized on an 64 processor ATHLON 1800+ Linux cluster.

Acknowledgment. We are grateful to the Bundesministerium für Bildung und Forschung (BMBF, grant 03C0356) for generous financial support.

Supporting Information Available: Experimental details, catalyst preparation and characterization, polymerization procedure, kinetics plot, and EDX measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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