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Supporting Information

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Variable Isotactic Poly(hydroxybutyrate)s by Ring-opening Polymerization of Racemic β-Butyrolactone using Achiral Cr^{III}(salophen)s

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

Experimental part

General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX500 and DRX400 instruments. Chemical shifts δ are given in ppm in reference to ^{1}H NMR and ^{13}C NMR signals of the deuterated solvents. Infrared measurements were obtained on KBr pellets using a Bruker IFS 113V and IFS 66V machine. MS spectra, CI or MALDI-Tof, were performed on a Finnigan MAT SSQ 7000 and a Bruker Daltonics REFLEX III spectrometer respectively (Sektion Massenspektrometrie, University of Ulm). 2,5-Dihydroxy-benzoicacid (DHB) was used as matrix for MALDI-Tof measurements. Elemental analyses were determined in the department of Analytical and Environmental Chemistry, University of Ulm. Infrared spectra were obtained on KBr pellets or liquid films using a Bruker IFS 113V and IFS 66V instrument. Molecular weight data were obtained from gel permeation chromatography (GPC) with $HCCl_3$ as solvent. The system consisted of μ-Styragel columns with a Waters 410 differential refractometer (Waters 150C ALC/GPC). For calibration, poly(styrene) standards with narrow molecular weight distributions were used (PSS). Thermal transitions of the polymer samples were monitored with a Perkin-Elmer DSC-7. Scan rates of 10 K/min (5) were used in the differential scanning calorimentry (DSC) experiments.

Materials: All chemicals were purchaised from Aldrich, Merck, Acros and Alfa Aesar and used as received. THF and β-butyrolactone were distilled from $LiAlH_4$ and CaH_2 respectively, chlorobenzene and toluene were dried over aluminum oxide. All solvents were degassed prior to use. Synthesis and polymerization reactions were performed under Argon as inert gas with standard Schlenck line techniques.

Complexes were synthesized in accord to literature procedures: **1a**[1], **1b-d:** analogous to **1a**, **2a**[2], **2b**[3].

General synthesis procedure (analogous to **1a**):

The phenylenediamine derivative and excess of the 3,5-di-*tert*-butylsalicylaldehyde (2.5 times) were refluxed in EtOH p.A. for several hours. The obtained yellow (**1d**) or orange (**1b**, **1c**) precipitate was filtered off, washed with EtOH p.A. and dried under high vacuum. If necessary recrystallized (from EtOH p.A.).

The ligand was transferred to a schlenck flask provided with 1.3 times of $CrCl_2$ under Argon. The mixture was dissolved in THF (absolute) and stirred for several hours under Argon atmosphere. The solution was allowed to stir under air over night. After the addition of 2,6-lutidine (2.6 times) the solution was stirred for another 2 hours at RT. The organic solution was diluted with *tert*-butylmethylether and washed three times with saturated NaCl and

NH_4Cl solutions respectively and dried over Na_2SO_4. The filtered solvent was evaporated and the obtained brown powder dried under high vacuum.

1b: N,N´-Bis(3,5-di-*tert*-butylsalicylidene)-4-chloro-1,2-phenylenediamine:

^1H NMR ($CDCl_3$, 400MHz): δ = 13.28, 13.18 (2s, 2H, OH); 8.57, 8.56 (2s, 2H, CH=N); 7.39-7.10 (7H, ArH); 1.36, 1.24 (4s, 36H, *t*Bu).

^{13}C NMR ($CDCl_3$, 400MHz): δ = 165.45, 164.95 (CN); 158.65, 158.58 (COH); 143.68, 141.42, 140.57, 140.50, 137.32, 137.29, 132.47, 128.70, 128.48, 127.02, 126.86, 120.79, 119.90, 118.26, 118.18 (Ar); 35.13 ($C(CH_3)$-*o*-COH); 34.17 ($C(CH_3)$-*p*-COH); 31.45 (CH_3-*p*-COH); 29.44 (CH_3-*o*-COH).

IR (KBr, cm^{-1}): 3441, 2955, 2908, 2867, 1614, 1594, 1568, 1481, 1467, 1438, 1391, 1361, 1321, 1271, 1248, 1200, 1170, 1123, 1090, 1026, 980, 925, 907, 880, 856, 826, 806, 770, 746, 727, 683, 642, 538, 506, 485.

Elemental analysis calcd (%) for $C_{36}H_{47}ClN_2O_2$ (575.24): C 75.17, H 8.24, N 4.87. Found: C 75.17, H 8.19, N 4.88.

MS (MALDI-Tof) for $C_{36}H_{47}ClN_2O_2$ (575.24): m/z: 575.6.

m.p. 203.5°C.

[N,N´-Bis(3,5-di-*tert*-butylsalicylidene)-4-chloro-1,2-phenylenediamine] chromium (III) chloride:

IR (KBr, cm^{-1}): 3554, 3394, 3068, 2954, 2904, 2866, 1637, 1614, 1599, 1575, 1548, 1524, 1481, 1461, 1425, 1384, 1359, 1329, 1255, 1235, 1196, 1170, 1124, 1085, 1023, 955, 929, 911, 871, 839, 805, 784, 746, 635, 588, 564, 538, 492, 463.

MS (CI): m/z: 659 [M^+], 624 [M^+-Cl], 572 [M^+-CrCl].

Elemental analysis calcd (%) for $C_{36}H_{45}CrCl_2N_2O_2$*1/2 THF*1/2 lutidine*H_2O (768.32): C 64.88, H 7.28, N 4.56. Found: C 65.06, H 7.54, N 4.73.

1c: N,N´-Bis(3,5-di-*tert*-butylsalicylidene)-4-bromo-1,2-phenylenediamine:

^1H NMR ($CDCl_3$, 400MHz): δ = 13.26, 13.17 (2s, 2H, OH); 8.56 (2s, 2H, CH=N); 7.39-7.03 (7H, ArH); 1.36, 1.24 (4s, 36H, *t*Bu).

^{13}C NMR ($CDCl_3$, 400MHz): δ = 165.43, 164.97 (CN); 158.64, 158.59 (COH); 143.90, 141.91, 140.58, 140.51, 137.30, 129.97, 128.72, 128.52, 127.03, 126.87, 122.77, 121.13, 120.13, 118.25, 118.17 (Ar); 35.12 ($C(CH_3)$-*o*-COH); 34.16 ($C(CH_3)$-*p*-COH); 31.44 (CH_3-*p*-COH); 29.41(CH_3-*o*-COH).

IR (KBr, cm^{-1}): 3440, 2954, 2907, 2866, 1613, 1592, 1564, 1482, 1466, 1438, 1391, 1361, 1321, 1271, 1247, 1199, 1170, 1119, 1084, 1025, 979, 919, 898, 880, 852, 825, 804, 770, 727, 682, 640, 537, 505, 483.

Elemental analysis calcd (%) for $C_{36}H_{47}BrN_2O_2$ (619.69): C 69.78, H 7.64, N 4.52. Found: C 69.80, H 7.69, N 4.52.

MS (MALDI-Tof) for $C_{36}H_{47}BrN_2O_2$ (619.69) : m/z: 619.4.

m.p. 207°C.

[N,N´-Bis(3,5-di-*tert*-butylsalicylidene)-4-bromo-1,2-phenylenediamine] chromium (III) chloride:

IR (KBr, cm^{-1}): 3553, 2954, 2927, 2904, 2866, 1637, 1615, 1596, 1575, 1546, 1523, 1479, 1463,1424, 1388, 1358, 1256, 1229, 1197, 1171, 1127, 1081, 1023, 953, 929, 890, 840, 784, 750, 721, 681, 635, 578, 539, 482, 416.

MS (CI): m/z: 705 [M^+], 670 [M^+-Cl], 618 [M^+-CrCl].

Elemental analysis calcd (%) for $C_{36}H_{45}BrCrClN_2O_2$*THF*1/2 lutidine*1/2 H_2O (812.78): C 62.21, H 7.02, N 4.17. Found: C 62.29, H 7.28, N 4.38.

1d: N,N´-Bis(3,5-di-*tert*-butylsalicylidene)-4-fluoro-1,2-phenylenediamine:

^{1}H NMR ($CDCl_3$, 400MHz): δ = 13.23 (s, 2H, OH); 8.56 (2s, 2H, CH=N); 7.39-6.89 (7H, ArH); 1.36, 1.25 (4s, 36H, *t*Bu).

^{13}C NMR ($CDCl_3$, 400MHz): δ = 165.48, 164.57 (CN); 158.65, 158.47 (COH); 140.55, 140.41, 139.15, 139.13, 137.32, 137.22, 128.68, 128.24, 126.99, 126.75, 120.77, 120.68, 118.29, 118.14, 113.84, 113.61, 106.99, 106.7 (Ar); 35.13 ($C(CH_3)$-*o*-COH); 34.18 ($C(CH_3)$-*p*-COH); 31.45 (CH_3-*p*-COH); 29.43 (CH_3-*o*-COH).

IR (KBr, cm^{-1}): 3437, 2958, 2908, 2868, 1617, 1582, 1491, 1479, 1439, 1394, 1325, 1270, 1252, 1230, 1204, 1170, 1151, 1096, 1028, 987, 966, 931, 878, 859, 818, 773, 690, 644, 496.

MS (MALDI-Tof) for $C_{36}H_{47}FN_2O_2$ (558.79): m/z: 559.4

[N,N´-Bis(3,5-di-*tert*-butylsalicylidene)-4-fluoro-1,2-phenylenediamine] chromium (III) chloride:

IR (KBr, cm^{-1}): 3554, 3401, 2955, 2902, 2866, 1641, 1608, 1583, 1548, 1525, 1494, 1461, 1425, 1386, 1359, 1329, 1266, 1234, 1200, 1168, 1131, 1096, 1023, 982, 953, 914, 871, 841, 803, 784, 747, 690, 636, 565, 539, 507, 489, 442, 420.

MS (CI): m/z: 643 [M^+], 608 [M^+-Cl], 556 [M^+-CrCl].

General polymerization procedure:

The appropriate amount of the catalyst **1a-d**, **2a, b** (23.05 mmol) was introduced to the schlenk tube under argon (Schlenk tubes have been oven dried and heated under reduced pressure prior to use). After addition of 3 ml β-butyrolactone (23.05 mol) the polymerization was performed at 100°C. After the desired polymerization time the reaction was allowed to cool down to room temperature. NMR sample in $CDCl_3$ was prepared to obtain the degree of conversion. If the reaction solution is too viscous (or solid) CH_2Cl_2 was used to solve the polymer before it is worked up. The polymer is precipitated out of Et_2O /n-hexane (50/150 ml). The product is filtered off (crystalline, isotactic product) or the liquid is decanted (oily, atactic polymer) and washed with Et_2O/n-hexane.

DFT calculations

Intensive DFT calculations were run to create and prove ideas about the active species. For investigations of stereocontrol, activation energy and reaction enthalpy of polymerization resulting in iso- or syndiotactic microstructures were compared.

The overall reaction mechanism like presented in Figure 2 was assembled due to the results of the stepwise DFT calculations. The first look has been done on the coordination of β-butyrolactone to the oxophilic Chromium atom. The results show that a free rotation of BL was possible and therefore no stereocontrol was obtained by selective coordination either by lactone ring-oxygen (Figure 3a) or carbonyl oxygen (Figure 3b) coordination.

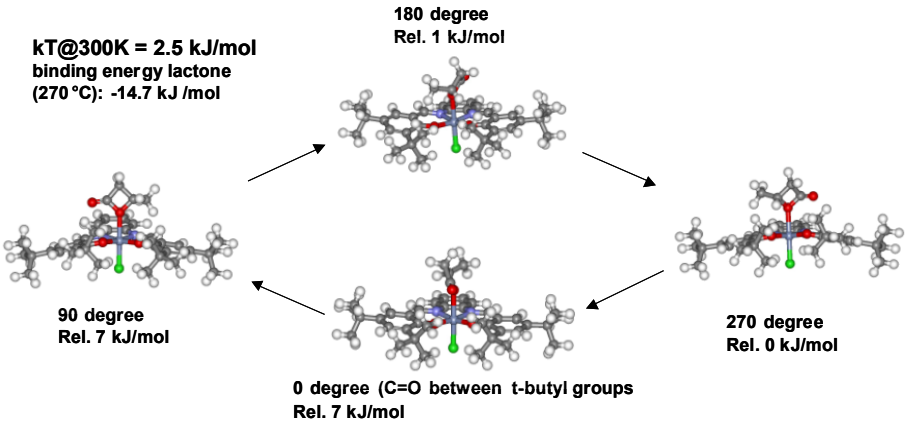

Figure 3a. Coordination of BL via lactone ring-oxygen

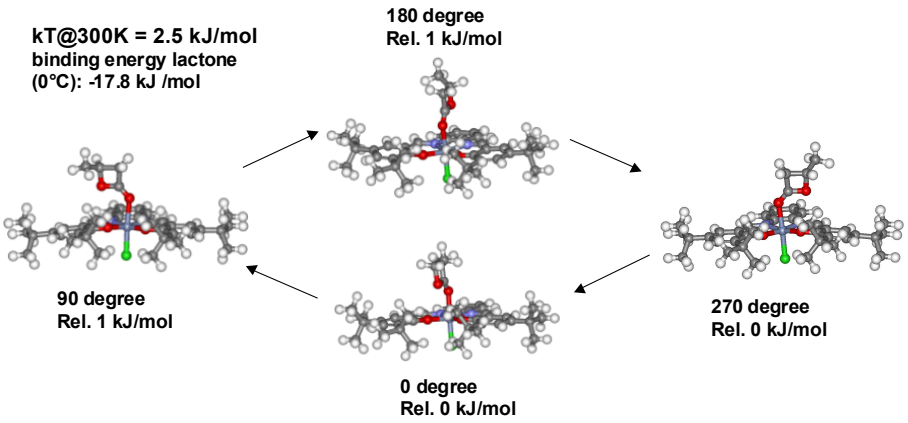

Figure 3b. Coordination of BL via carbonyl oxygen

In the next step the focus was set on the ring-opening reaction by the nucleophilic chloride. Depending on the two above mentioned coordination types the possible initiations to result in carboxylate or alkoxide species were investigated (Figure 4). Results clearly indicated that a carboxylate is much more likely. Even if an alkoxide was formed in the first step, insertion of another monomer gave a carboxylate again. All three possible initiation pathways are shown in Figure 5a-c. The reaction with is most favored is the attack of the C-Me atom by the chloride when the BL is coordinated through the ring-oxygen resulting in a carboxylate species.

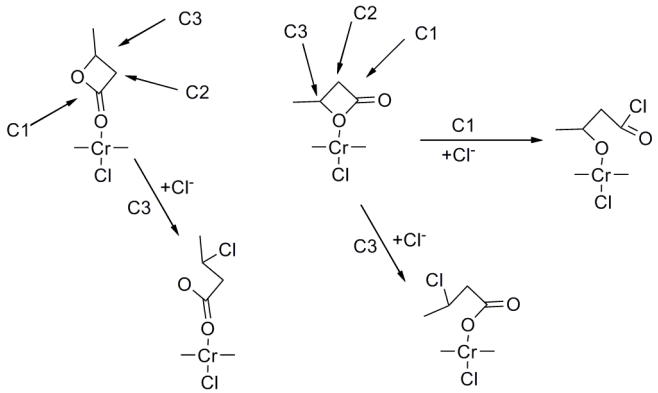

Figure 4. Possible initiation reactions

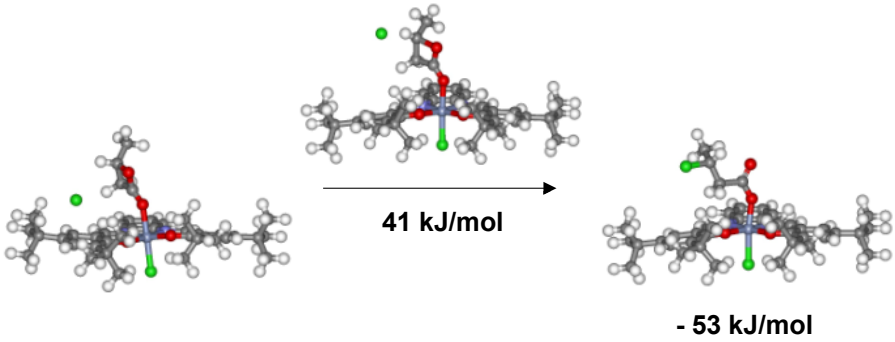

Figure 5a. Initiation reaction of carbonyl O coordinated BL with chloride (attack at C-Me C3 results in Cr carboxylate)

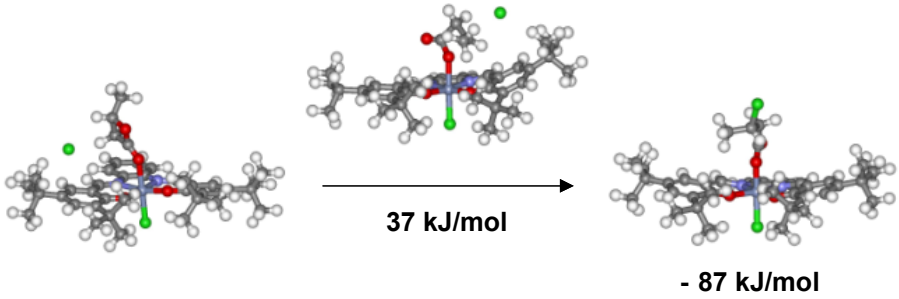

Figure 5b. Initiation reaction of ring-O coordinated BL with chloride (attack at C-Me C3 results in Cr carboxylate)

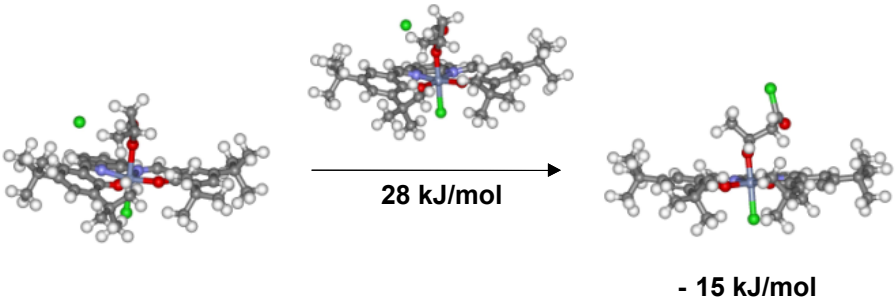

Figure 5c. Initiation reaction of ring-O coordinated BL with chloride (attack at carbonyl-C C1 results in Cr alkoxy)

The next step is ring opening reaction with a carboxylate, which presents a growing polymer chain. In Figure 6 a general scheme is given. Calculations with possible stereosequences (S,R and S,S) were run. The attack of a free carbonylate to BL and to BL coordinated to a Chromium atom have been investigated. The uncatalyzed reaction had high activation energy (70 $kJmol^{-1}$), however, the addition of Cr salophen lowered the activation barrier significantly by 50-60 $kJmol^{-1}$. Due to formation of a Cr oxygen bond the reaction is strongly exotherm (-100 $kJmol^{-1}$) (Figure 7). But no model was able to describe the reason for stereoselectivity (Table 2).

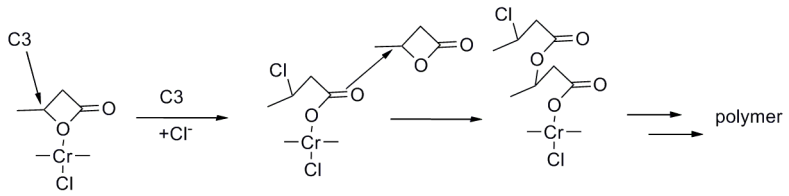

Figure 6. Ring opening reaction to polyester

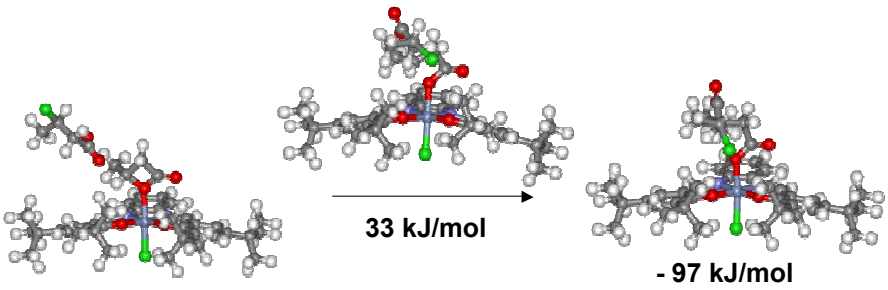

Figure 7. Ring opening reaction of coordinated BL with carboxylate

Table 2. Ring opening reaction of R- and S-carboxylate with Cr coordinated R- and S-lactone

carboxylate	lactone	E_A [kJmol^{-1}]	E_r [kJmol^{-1}]
R	R	33	-97
R	R (180°)	19	-108
R	S	19	-110
R	S (180°)	18	-116
S	R	13	-119
S	R (180°)	19	-110
S	S	19	-108
S	S (180°)	18	-118

Our proposed mechanism of stereoselective ring-opening polymerization of beta-butyrolactone involves a sandwich-like arrangement of two Cr salophen complexes. In Figure 8 a general scheme of the mechanism is shown. One Cr atom carries the growing polymer chain as a Cr carboxylate. The second Cr salophen is coordinated to a chiral BL. Somehow the local arrangement of the two salophen complexes favors the incorporation of a S-BL following the other enantiomer. As the chiral C-atom of the growing polymer chain is quite far away from the Cr atom, a kind of secondary sterical control must exist.

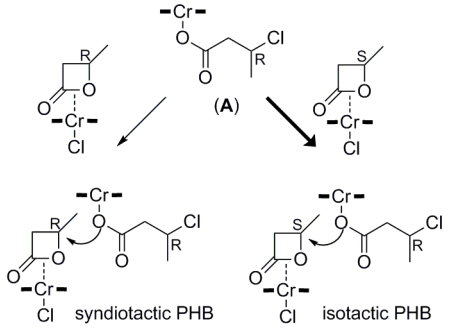

Figure 8. Proposed mechanism of polymerization resulting in isotactic PHB

Starting with reduced models, a possible reaction pathway was identified. In Figure 9 the reaction is shown for the full Cr salophen complexes. The reaction occurs in a kind of cage made by to planar salophen complexes. The

complexes are arranged in that way that the bulky tert. butyl groups show in the opposite direction to limit sterical interaction.

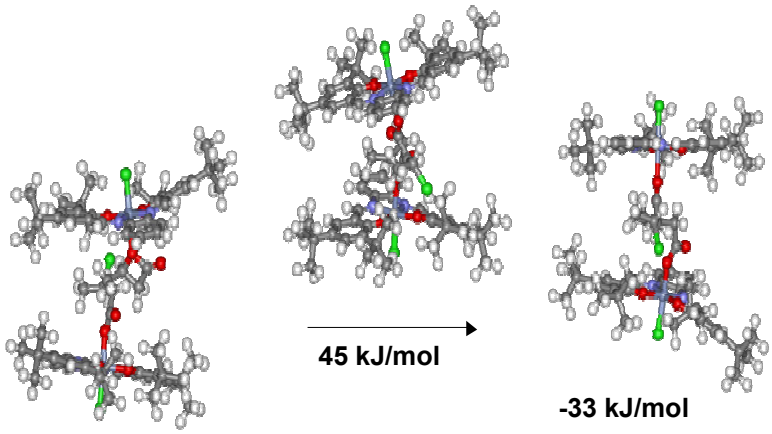

Figure 9. Polymerization of beta-butyrolactone via Cr salophen sandwich

Calculations were run with different stereosequences (Table 3). DFT calculations were not capable to distinguish between the 2 possible reactions. Nevertheless, a careful look on the 3D-models showed that the interaction of the methyl group of the lactone with the polymer chain would favor an isotactic polymer chain (Figure 10).

Table 3. Ring opening reaction of R- and S-Cr-carboxylate with Cr cooridnated R- and S-lactone

carboxylate	**lactone**	E_A [kJmol^{-1}]	E_r [kJmol^{-1}]
R	R	45	-33
R	S	41	-36

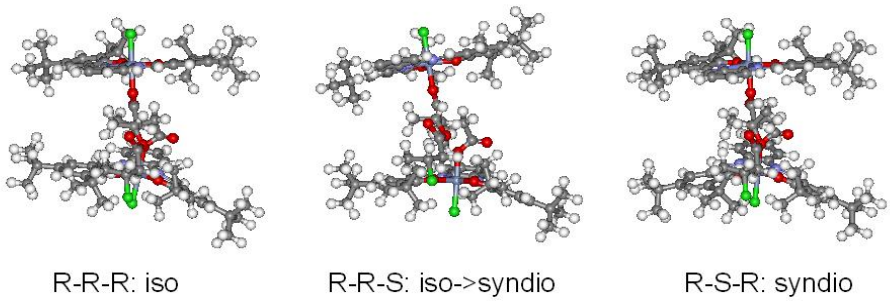

Figure 10. Cr salophen sandwich arrangements with different stereosequences

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 transition state (TS) and the associated reactants and products. The nature of all transition states was verified (only one negative eigenvalue of the hessian). Reactants and products were identified 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.[4] DFT methodology was used at the B-P86/SV(P)[5] level of theory to locate all stationary points. Single-point energy calculations were carried out using the TZVP[6] basis set. Geometries were optimized on an 64 processor ATHLON 1800+ Linux cluster.

References

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