Polymerization Catalysis

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Stereospecific Styrene Enchainment at a Titanium Site within a Helical Ligand Framework: Evidence for the Formation of Homochiral Polystyrene**

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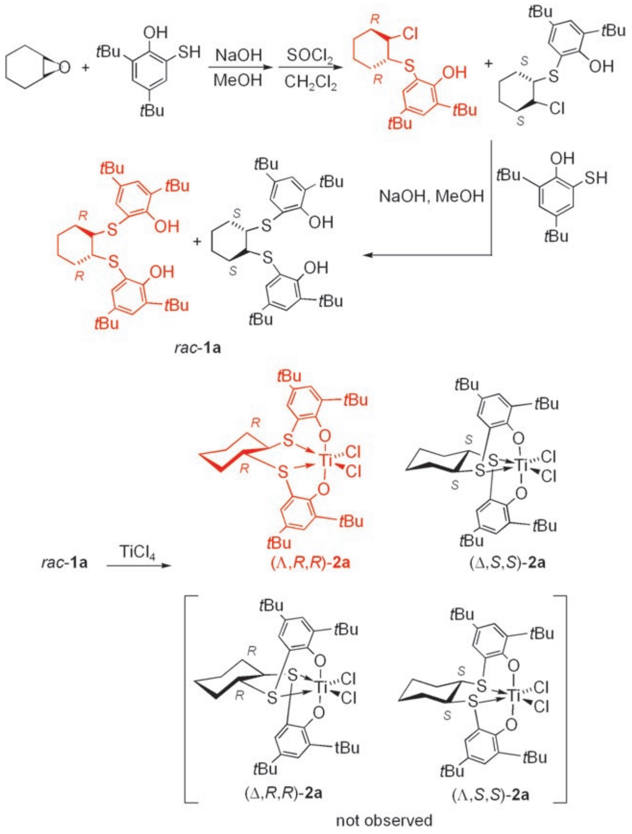
The phenomenon of cryptochirality renders isotactic poly(α-olefin)s such as polypropylene optically inactive, since C_s symmetry can be assumed for high-molecular-weight polymers formed from prochiral olefins.[1,2] Only for highly specific sequences of segments within the poly(α-olefin) chain can optical activity be measured.[3,4] The advent of chiral, and in rare cases optically active, enantiomerically pure ansa-zirconocene catalysts with well-defined molecular structure[5] allowed the observation of the stereochemical discrimination of the prochiral monomer at a single metal center during oligomerization.[2,6,7] To the best of our knowledge, it has not yet been determined at what degree of polymerization the observable optical activity of poly(α-olefin)s disappears and whether "homochiral" isotactic poly(α-olefin)s can be accessed.

We have recently shown that configurationally rigid bis(phenolato) titanium catalysts derived from linear [OSSO]-type ligands efficiently polymerize styrene to give isotactic polystyrene (iPS).[8] iPS was previously prepared using heterogeneous Ziegler-type catalysts and characterized as the first crystallizable poly(α-olefin) by Natta et al.[9] We have now prepared optically active variants of the above-mentioned catalyst precursors. By utilizing chain-transfer methodology in the presence of 1-hexene, we demonstrate that the insertion of styrene in such postmetallocene catalysts[10] occurs stereospecifically giving optically active iPS oligomers.

As we reported previously, the stereorigidity of the titanium catalysts containing a [OSSO]-type ligand depend rather critically on the presence of a two-carbon backbone linking the two phenol units and on the presence of bulky *ortho* substituents.[11] Therefore, we introduced a *trans*-1,2-cyclohexanediyl backbone that connects two 4,6-di-*tert*-butylphenol (**a**) or 6-*tert*-butyl-4-methylphenol (**b**) groups by a SCCS link. We followed the reaction sequence delineated in Scheme 1 and obtained the bis(phenol) *rac*-**1a** in three steps. Starting with cyclohexene oxide, consecutive nucleophilic



Scheme 1. Synthesis of the chiral catalyst precursors **2a**.

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substitutions by the mercaptophenolate were critical to the successful synthesis, which made use of anchimeric assistance in each of the substitution steps. Chiral resolution of *rac*-**1a** was achieved by fractional crystallization and column chromatography of the bis((1*S*)-camphor sulfonate)s, for which both diastereomers were isolated and their absolute configurations determined by X-ray crystallography. After hydrolytic removal of the chiral auxiliary, the enantiomerically pure bis(phenols) (−)-(*R*,*R*)-**1a** and (+)-(*S*,*S*)-**1a** were obtained in good yield and characterized by their optical rotation and CD spectra (see the Supporting Information). Complexation of these ligands at a TiX_2 fragment (**2**: X = Cl, **3**: X = O*i*Pr) was straightforward by reaction of the bis(phenol) with TiX_4.

Use of the racemic ligand *rac*-**1a** resulted in single crystals for the dichloro complex **2a**. According to X-ray crystallography, the chiral backbone led to the formation of a single configuration (helicity) at the titanium center. Thus, the racemic ligand derived from *rac*-**1a** resulted in the selective formation of only one enantiomeric pair of the diastereomeric complex ((Λ,*R*,*R*)-**2a** and (Δ,*S*,*S*)-**2a**); the other possible diastereomers ((Δ,*R*,*R*)-**2a** and (Λ,*S*,*S*)-**2a**) were absent (Figure 1).[12] When we employed the resolved, enantiomerically pure bis(phenol)s (−)-(*R*,*R*)-**1a** and (+)-(*S*,*S*)-**1a**, the corresponding enantiomerically pure titanium complexes (Λ,*R*,*R*)-**2a** and (Δ,*S*,*S*)-**2a** were obtained and completely characterized. Specific rotations of $[\alpha]_D^{23} = -277.3\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ for (Λ,*R*,*R*)-**2a** and $+277.3\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ for (Δ,*S*,*S*)-**2a** ($c = 0.002\ \mathrm{g\,mL^{-1}}$, CH_2Cl_2), CD spectra (Figure 2), and a single-crystal structure determination confirm the chiral structure, in which the tetradentate ligand is arranged helically around the octahedral titanium center.

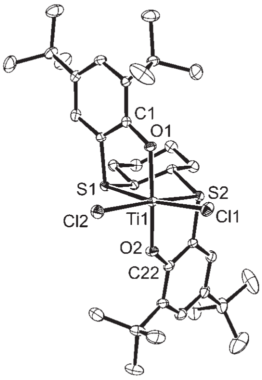


Figure 1. Structure of the Δ,*S*,*S* enantiomer in the crystal of the racemic compound **2a** (hydrogen atoms omitted; atoms depicted at the 50% probability level). Selected bond lengths [Å] and angles [°]: Ti–Cl 2.2639(7), 2.2733(7), Ti–S 2.6106(7), 2.6191(7) Ti–O 1.8639(16), 1.8827(16); Cl-Ti-Cl 108.38(3), O-Ti-O 157.93(7), S-Ti-S 79.91(2).

Following our previous studies on homogeneous styrene polymerization,[8,11] the enantiomeric pairs of titanium catalyst precursors **2a** were activated by methylaluminoxane (MAO) (to give a configurationally stable alkyl cation with homotopic sites[11b]) and allowed to polymerize styrene. As expected, the isotactic polystyrene obtained showed no optical rotation. After considerable efforts to find a suitable chain-transfer agent (H_2, AlR_3, ZnR_2)[13] we found chain termination using 1-hexene to be most practical.[14] By variation of the styrene/1-hexene ratio, a series of oligostyrenes was synthesized using both enantiomers of the precatalyst **2a** in toluene (Scheme 2, Table 1). A typical pair of oligomers having M_n of approximately 2000 (runs 5 and 6, Table 1) showed peaks assignable to chains containing one to five 1-hexene units ($m = 0$–4) attached to a polystyrene segment (maximum at $n \approx 30$) in the MALDI TOF mass spectra (see the Supporting Information). ^1H and ^{13}C NMR spectra confirmed the presence of iPS segments terminated by regio- and stereoirregular oligo(hexene) segments. Homo-oligomerization of 1-hexene using the same catalyst system confirmed the formation of oligo(1-hexene) showing the absence of both regio- and stereoselectivity as well as optical activity.

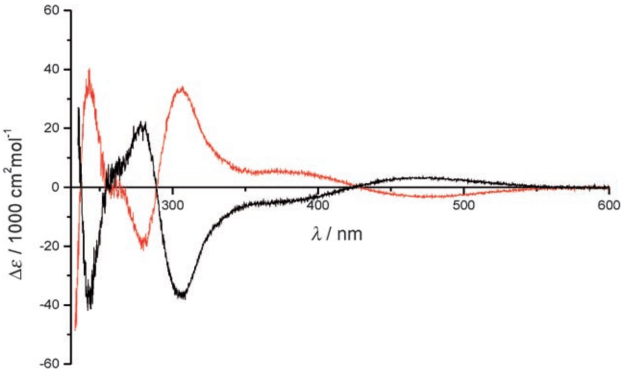
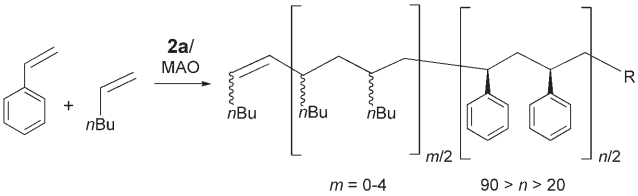


Figure 2. CD spectra of the enantiomerically pure titanium complexes (−)-(Λ,*R*,*R*)-**2a** (red line) and (+)-(Δ,*S*,*S*)-**2a** (black line) in CH_2Cl_2 at 25 °C.



Scheme 2. Synthesis of isotactic polystyrene oligomer.

The dependence of the specific rotation values on the molecular weight of the iPS is depicted in Figure 3. It is evident that for $M_n > 5000$ no optical activity could be detected, but below this threshold (corresponding to roughly 45 styrene units with an average of three terminal 1-hexene units) specific rotation $[\alpha]_D^{23}$ of $\pm 1.5(1)$–$5.9(1)\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ could be measured reproducibly.[15] Moreover, each enantiomeric titanium catalyst produced only oligomers with the same sign of optical rotation, corroborating that enantiomorphic site control is operative. It is noteworthy that for the samples of the lowest molecular weights (runs 1 and 2, Table 1), a decrease in optical rotation is observed. Although we were unable to produce samples of lower molecular weight, we ascribe this effect to the lower stereoselectivity at the earlier stages of insertion, as efficient enantiofacial discrimination of styrene is effected by the

Table 1: Isotactic polystyrene with oligo(1-hexene) terminal groups prepared by using MAO-activated, optically active (−)-(Λ,*R*,*R*)-**2a** and (+)-(Δ,*S*,*S*)-**2a**.

Run[a]	[Styrene] [mol L^{-1}]	[1-hexene] [mol L^{-1}]	Cat.[b]	Yield [mg]	M_n[c] [g mol^{-1}]	M_w/M_n[c]	$[\alpha]_D^{23}$[d] [deg cm^3 g^{-1} dm^{-1}]	$[\Phi]_D^{23}$ [deg cm^2 kmol^{-1}]
1	0.48	4.5	(*R*,*R*)-**2a**	494	750	1.24	−4.9(1)	−37
2	0.48	4.5	(*S*,*S*)-**2a**	568	790	1.35	+4.4(1)	+35
3	0.64	4.5	(*R*,*R*)-**2a**	517	870	1.31	−5.9(1)	−45
4	0.64	4.5	(*S*,*S*)-**2a**	377	1120	1.25	+5.6(1)	+61
5	1.6	4.5	(*R*,*R*)-**2a**	325	1930	1.46	−4.2(2)	−81
6	1.6	4.5	(*S*,*S*)-**2a**	468	1880	1.49	+3.5(2)	+65
7	1.6	3.4	(*R*,*R*)-**2a**	153	2700	1.46	−2.9(1)	−78
8	1.6	3.4	(*S*,*S*)-**2a**	168	2680	1.46	+2.7(1)	+73
9	1.6	2.3	(*R*,*R*)-**2a**	221	3750	1.52	−2.5(1)	−94
10	1.6	2.3	(*S*,*S*)-**2a**	235	3460	1.58	+2.2(1)	+74
11	1.6	1.4	(*R*,*R*)-**2a**	567	4420	1.67	−1.8(1)	−80
12	1.6	1.4	(*S*,*S*)-**2a**	617	4590	1.45	+1.5(1)	+67
13	3.2	3.2	(*R*,*R*)-**2a**	517	5930	1.68	±0	±0
14	3.2	3.2	(*S*,*S*)-**2a**	680	5870	1.68	±0	±0

[a] Reaction time for runs 1–6: 6 h. [b] Activated by MAO. [c] Determined by GPC using polystyrene standard. [d] $c = 0.01$ g mL^{-1} in CH_2Cl_2.

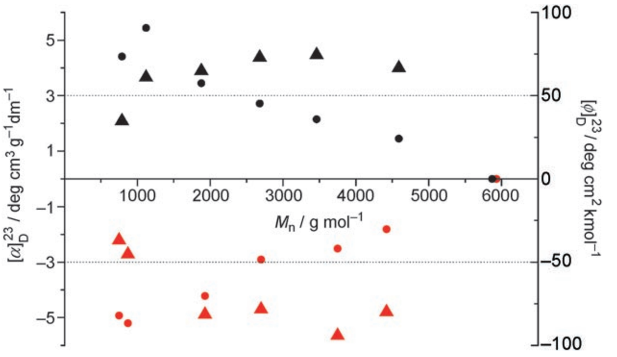


Figure 3. Dependence of the specific rotation $[\alpha]_D^{23}$ and molar rotation $[\Phi]_D^{23}$ on the number-averaged molecular weight of isotactic oligostyrene terminated by 1-hexene. Specific rotation (●) and molar rotation (▲) of samples prepared with the complex (−)-(Λ,*R*,*R*)-**2a**; (●) optical rotation and molar rotation (▲) of samples prepared with the complex (+)-(Δ,*S*,*S*)-**2a**.

interplay of the growing chiral chain and the stereorigid ligand sphere. There appears to be an agreement of the molar rotation value $[\Phi]_D^{23}$ of approximately −70 deg cm^2 kmol^{-1} ($CHCl_3$) for oligomers prepared using (Λ,*R*,*R*)-**2a** with the $[\Phi]_D^{30}$ value of −85.7 deg cm^2 kmol^{-1} ($CHCl_3$) reported for the model compound (−)-(2*R*,4*R*)-2,4-diphenylpentane.[16,17]

In conclusion, we have demonstrated that configurationally stable, enantiomerically pure titanium postmetallocene catalysts are capable of producing isotactic oligostyrenes that show measurable optical activity up to a degree of polymerization of 45. We are currently investigating the absolute stereoselectivity of the insertion of the prochiral monomer into the titanium–alkyl bond within the helical coordination sphere.[17]

Experimental Section

rac-**2a**: Neat titanium tetrachloride (0.08 g, 0.43 mmol) was added dropwise to a solution of the racemic bis(phenol) *rac*-**1a** (0.24 g, 0.43 mmol) in 30 mL of pentane at −10 °C; the mixture was warmed to room temperature and stirred for 2 h. A red powder precipitated that was decanted off, washed twice with 15 mL of pentane, and dried in vacuo to give *rac*-**2a** (0.25 g, 0.37 mmol); yield: 86 %. ^{1}H NMR: δ = 0.36 (m, 2H, CH (C_6H_{10})), 1.07–1.18 (m, 2H, CH (C_6H_{10})), 1.18 (s, 18H, $C(CH_3)_3$), 1.23–1.43 (m, 2H, CH (C_6H_{10})), 1.57 (s, 18H, $C(CH_3)_3$), 1.72–1.85 (m, 2H, CH (C_6H_{10})), 2.43–2.56 (m, 2H, SCH), 7.08 (d, 2H, $^4J_{HH}$ = 2.3 Hz, arom. CH (C3)), 7.45 ppm (d, 2H, $^4J_{HH}$ = 2.3 Hz, arom. CH (C5)). ^{13}C{^{1}H} NMR: δ = 25.10 (CH_2 (C_6H_{10})), 29.82 ($C(CH_3)_3$), 31.59 ($C(CH_3)_3$), 32.41 (CH_2 (C_6H_{10})), 34.61 ($C(CH_3)_3$), 35.87 ($C(CH_3)_3$), 55.59 (SCH), 117.42 (arom. C2), 127.33 (arom. C3), 129.70 (arom. C5), 137.18 (arom. C4), 144.03 (arom. C6), 167.64 ppm (arom. C1). Analysis (%) calcd for $C_{34}H_{50}Cl_2O_2S_2Ti$ (673.66): C 60.62, H 7.48; found: C 60.63, H 7.86. Crystals suitable for X-ray analysis were obtained as toluene solvate by slow evaporation of a toluene solution at room temperature.[18]

General polymerization procedure: A Schlenk tube was charged with toluene (calculated for a total volume of 15 mL), 1.2 mL of a MAO solution in toluene (10 wt %; Eurecen; used as received), and a mixture of styrene and 1-hexene (toluene, styrene and 1-hexene were dried over sodium or calcium hydride and degassed three times before use; concentrations of the monomers are given in Table 1). This mixture was stirred for 20 min at 40 °C, followed by addition of 0.5 mL of a 0.25 µM stock solution of the enantiomerically pure complex (−)-(*R*,*R*)-**2a** or (+)-(*S*,*S*)-**2a** (17 mg, 25 µmol) in 10 mL of toluene. The reaction mixture was stirred at 40 °C for 2 h, the reaction quenched by addition of 0.5 mL of isopropyl alcohol, and the polymer precipitated from 100 mL of acidified methanol. The product was redissolved in chloroform and precipitated again from acidified methanol. This procedure was repeated after filtration of the chloroform solution through a layer of silica. The oligomers were dried in vacuo for several hours.

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[17] A molecular model based on a so-called octant scheme by Pino et al.[2] suggests that at a Λ,*R*,*R* titanium site, styrene inserts via the *si* (pro-*R*) face with secondary regiochemistry, resulting in a chain of *R* configurations; likewise styrene inserts at a Δ,*S*,*S* titanium site via the *re* (pro-*S*) face forming in a chain of *S* configurations.

[18] X-ray crystal structural data for complex *rac*-**2a**: $C_{75}H_{108}Cl_4O_4S_4Ti_2$, $M_r = 1439.45$, $T = 110$ K, crystal dimensions $0.3 \times 0.3 \times 0.2$ mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 9.9475(9)$, $b = 30.095(3)$, $c = 26.477(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.385(2)°$, $Z = 4$, $U = 7796.6(12)$ Å^3, $\rho_{calcd} = 1.226$ g cm^{-3}, $\mu = 0.494$ mm^{-1}, 114914 collected, 21765 unique ($R_{int} = 0.0619$), final $R_1 = 0.0618$, wR_2 $[I > 2\sigma(I)] = 0.1178$, residual electron density extremes were 0.536 and -0.379 e Å^{-3}. CCDC-637376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.