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Stereospecific post-metallocene polymerization catalysts: the example of isospecific styrene polymerization

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Abstract

In the context of developing single-site stereoselective post-metallocene catalysts, the case for isospecific styrene polymerization catalysts based on methylaluminoxane-activated group 4 metal bis(phenolato) complexes is summarized. Ligands derived from the 1,4-dithiabutanediyl-linked bis(phenol)s have been found to induce stereochemical rigidity by the presence of the hemi-labile sulfide donor functions. Isospecific styrene polymerization was achieved using easily accessible catalyst precursors of the type $[MX_2(OC_6H_2\text{-}^tBu_2\text{-}4,6)_2\{S(CH_2)_2S\}]$ (M = Ti, Zr, Hf; X = Cl, O^{i}Pr, CH$_2$Ph). Activating the dibenzyl titanium complex $[Ti(CH_2\text{-}Ph)_2(OC_6H_2\text{-}^tBu_2\text{-}4,6)_2\{S(CH_2)_2S\}]$ with $B(C_6F_5)_3$ and Al^{i}Bu$_3$, controlled isotactic polymerization became possible at lower temperatures. A remarkable dependence of both the activity and stereoselectivity on the ligand substitution pattern was observed. Analogous precursors with the 1,5-dithiapentanediyl-linked bis(phenolato) ligand gave syndiotactic polystyrene with lower activity.
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Keywords: Titanium; Styrene polymerization; Stereoselectivity; Stereorigidity; Post-metallocene catalysts

1. Introduction

One of the most important contributions organometallic chemistry has made in the area of coordinate polymerization relates to the understanding of the stereocontrol on the molecular level during propylene polymerization using rationally designed zirconocene precatalysts [1,2]. Currently there is considerable activity in developing stereospecific polymerization catalysts which do not feature the ubiquitous bis(η^5-cyclopentadienyl) ligand framework [3]. However, it is now recognized that the symmetry-related control of the stereoselectivity by rationally designed ligand spheres for the catalytically active metal center becomes highly challenging, once the bent metallocene structure is abandoned [4]. In Chart 1 a selection of recent stereoselective single-site polymerization catalyst precursors are collected.

Interestingly, there have so far been no general ways to control the stereoselectivity during the polymerization of the commodity monomer styrene [5]. Syndiotactic polystyrene, discovered by Ishihara et al. at Idemitsu [6], is produced by trivalent mono(cyclopentadienyl)titanium catalysts of the type $[Ti(\eta^5\text{-}C_5R_5')R]^+$ [7]. It has recently been commercialized as a new high melting, fast crystallizing, chemically resistant thermoplastic (Xarec®). The virtually perfect syndiotacticity resulting

Chart 1.

2. Results and discussion

Titanium complexes with a 2,2′-sulfur-bridged bis(phenolato) ligand of the type [Ti{(OC$_6$H$_2$-^{t}Bu-6-Me-4)$_2$S}X$_2$] have been introduced as one of the early examples for post-metallocene catalyst precursors [12a]. They also show activity in syndiospecific styrene polymerization upon activation with methylaluminoxane [12]. The report on isospecific living 1-hexene polymerization by a diamine-bis(phenolato) zirconium catalyst as well as other structurally defined stereospecific post-metallocene catalysts [9] intrigued us to find new styrene polymerization catalysts with controllable stereoregulating property. We prepared two new bis(phenols), (HOC$_6$H$_2$-^{t}Bu$_2$-4,6)$_2${S(CH$_2$)$_n$S} **1a** (n = 2) and **1b** (n = 3), with a 1,ω-dithiaalkanediyl bridge, by nucleophilic substitution of the corresponding 1,ω-dibromoalkane by 3,5-di-*tert*-butyl-2-hydroxybenzenethiol [13]. Initial attempts to obtain stereorigid bis(phenolato) titanium complexes were not successful, since the linked bis(phenolato) ligand frameworks were fluxional [12c,14].

Reaction of **1a** with titanium tetrachloride or titanium tetra(isopropoxide) in toluene cleanly afforded the corresponding complexes **2a** and **3a** in quantitative yield (Scheme 1). The bis(phenol) with the longer 1,5-dithiapentane-link **1b** analogously gave the titanium complexes **2b** and **3b** in quantitative yield (Scheme 2). These complexation reactions were found so clean that they can be easily adapted for automated syntheses.

According to NMR spectra, the dichloro titanium complex with the 1,4-dithiabutane-link **2a** differs from the 1,5-dithiapentane-linked bis(phenolato) complex **2b** by its configuration. All NMR spectroscopic data of the complexes **2a** and **3a** indicate molecular C_2-symmetry, which is evident from the symmetry-related phenolate rings and the presence of an AB spin pattern for the CH$_2$ units in the bridge. Zirconium and hafnium dibenzyl complexes **4a** and **5a**, obtained by the reaction of **1a** with zirconium and hafnium tetrabenzyl, show an additional AB pattern for the CH$_2$ groups due to the two *cis*-benzyl ligands. Furthermore, the temperature
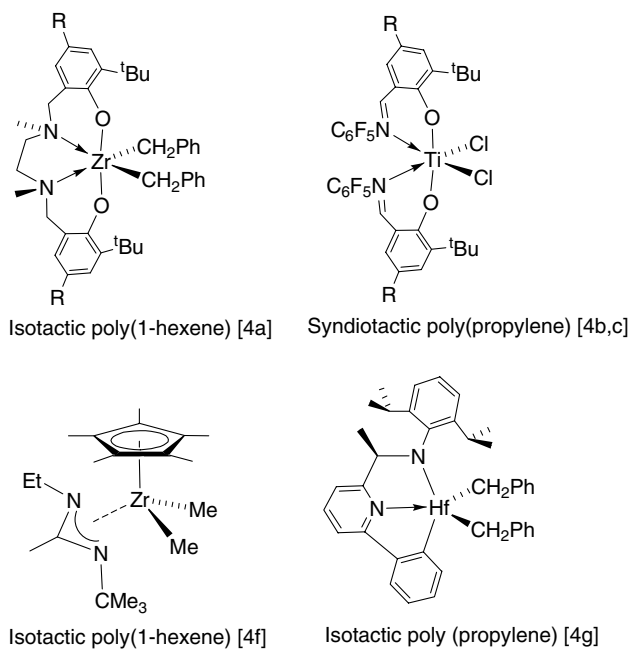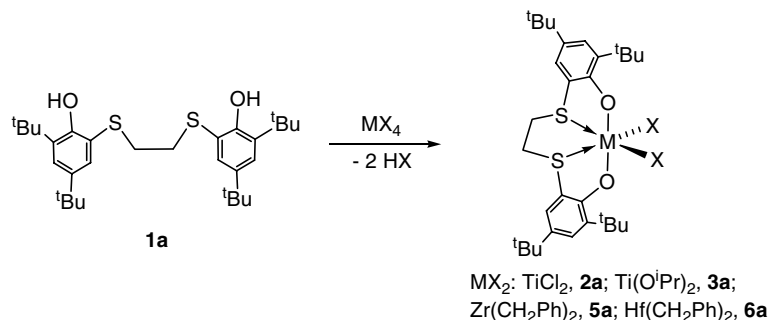
in high crystallinity, however, could not be rationally influenced by ligand design, causing problems of brittleness during processing. Isotactic polystyrene, known for almost half a century and initially noted for its crystallinity, is still best produced by heterogeneous Ziegler–Natta catalysis [8–10]. Except for detailed works by Tkatchenko et al. on isospecific oligostyrenes using phosphine-supported nickel cations [10] and for a recent report on isospecific styrene polymerization by isopropylidene-linked Brintzinger-type zirconocenes by Arai et al. [9] the synthesis of isotactic polystyrene by single-site organometallic catalysts was virtually unknown. Recently, a family of structurally well-characterized post-metallocene group 4 metal catalyst precursors that efficiently polymerize styrene to give isotactic polystyrene was discovered [11]. We summarize here some salient feature of these new stereoselective catalyst precursors.

Isotactic poly(1-hexene) [4a]
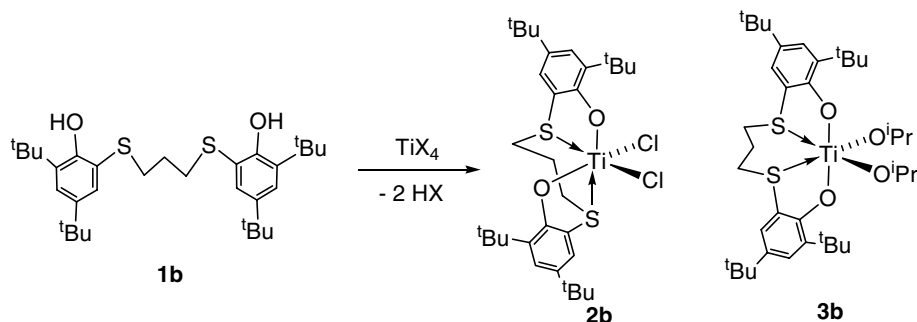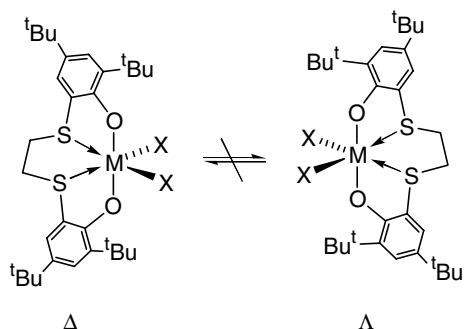
Syndiotactic poly(propylene) [4b,c]

Isotactic poly(1-hexene) [4f]

Isotactic poly (propylene) [4g]

Scheme 1.

MX$_2$: TiCl$_2$, **2a**; Ti(O^{i}Pr)$_2$, **3a**;
Zr(CH$_2$Ph)$_2$, **5a**; Hf(CH$_2$Ph)$_2$, **6a**

Scheme 2.

Scheme 3.

invariance of the NMR spectra suggests significant configurational stability in solution (Scheme 3).

Crystallographic structure determination of an analogue of **2a** [TiCl$_2$(OC$_6$H$_2$-^{t}Bu-6-Me-4)$_2${S(CH$_2$)$_2$S}] (**2a'**) confirms that this complex adopts a C_2-symmetrical configuration with *cis*-arranged chloro (Cl–Ti–Cl

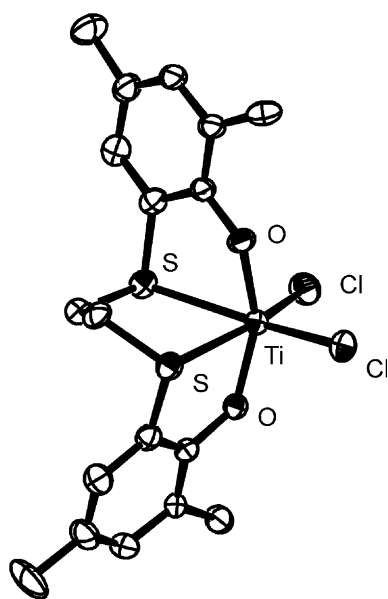103.4(1)°) and thioether groups (Ti–S1 2.647(3), Ti–S2 2.647(3) Å). Fig. 1 depicts the molecular structure for the Δ configurational isomer. The two sulfur atoms of the link, which shows a gauche conformation with dihedral angle SCCS of 54.5(10)°, evidently enforce the *trans*-coordination of the two bulky phenolato ligand moieties. Without the sulfur coordination, the coordination geometry would be tetrahedral and consequently non-chiral.

In contrast, **2b** shows at room temperature a pattern of broad signals due to fluxional behavior. The low-temperature ^{1}H NMR spectrum can be explained by an unsymmetrical structure. The crystallographic analysis shows that **2b** adopts a C_1-symmetric structure in which one sulfur atom is disposed *trans* to the chloro and another *trans* to the oxygen atom, resulting in *cis*-coordinated phenolato groups (Fig. 2). Notably the structure of the di(isoproxy) complex is similar to that of **3a**

Fig. 1. Molecular structure of the Δ isomer of **2a'**. Methyl groups of the 6-*tert*-butyl groups have been omitted.
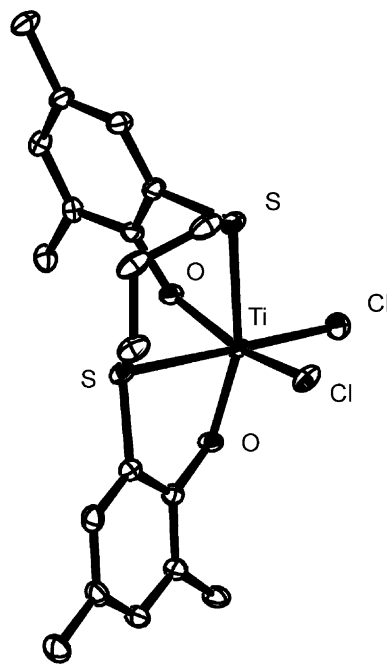

Fig. 2. ORTEP diagram of the molecular structure of **2b**. Methyl groups of all the *tert*-butyl groups have been omitted.

(*trans*-O,O, *cis*-S,S), indicating that for the 1,5-dithiapentane-linked bis(phenolato) complexes more than one preferred configuration is observed. The interconversion between the C_2-symmetric (*trans*-O,O, *cis*-S,S) and C_1-symmetric (*cis*-O,O, *cis*-S,S) configuration can be imagined as a flipping of one of the OTiS five-membered chelate rings (Scheme 4). For the longer and conformationally more flexible 1,5-dithiapentane-link this process is obviously more facile. This is borne out by theoretical calculations which show that the energy barrier to this isomerization is considerably lower for the 1,5-dithiapentane- than for the 1,4-dithiabutane-link.
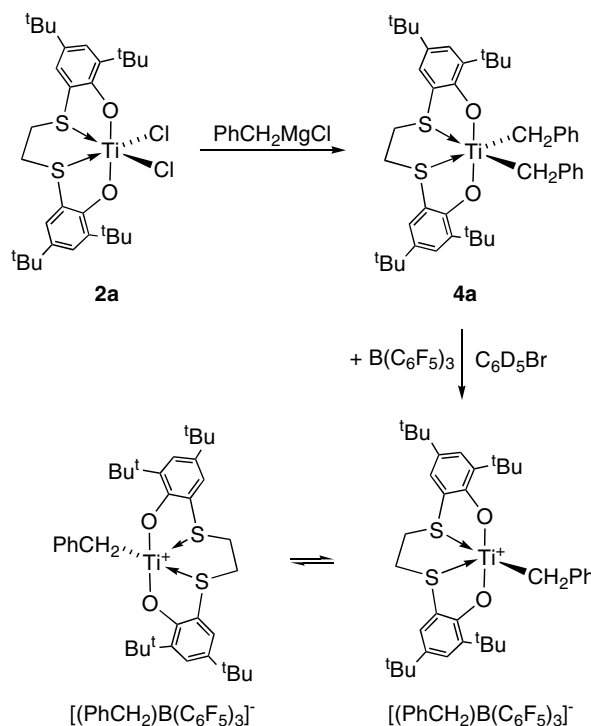
Upon activation with excess methylaluminoxane (MAO), the complexes **2a–5a** were found to be active for isospecific styrene polymerization, whereas **2b** and **3b** exhibit low activity for syndiospecific polymerization toward styrene. The polymerization results are summarized in Table 1. The 1,5-dithiapentane-bridged complexes **2b** and **3b** are one order of magnitude less active than the 1,4-dithiabutane-bridged derivatives **2a** and **3a**. Melting temperatures, data from WAXS analysis, and NMR spectroscopy unambiguously show that the polystyrenes produced in runs 1–6 have isotactic microstructure, whereas the polystyrenes produced in runs 7 and 8 have syndiotactic microstructure [15]. Gel permeation chromatographic analysis of the isotactic
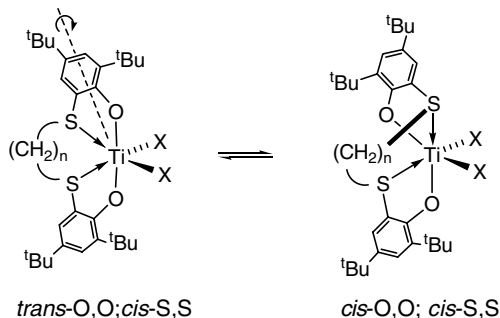
polystyrenes shows polydispersity indices of ca. 2, indicative of single-site catalysis.

As active species, we assume an alkyl cation [TiR-$(OC_6H_2$-$^tBu_2$-4,6)$_2${S(CH$_2$)$_2$S}]$^+$ in analogy to similar non-metallocene polymerization catalysts [10]. The dichloro titanium complex **2a** can be smoothly converted into the dibenzyl complex [Ti(CH$_2$Ph)$_2$(OC$_6$H$_2$-$^tBu_2$-4,6)$_2${S(CH$_2$)$_2$S}] (**4a**) which according to NMR spectroscopic analysis gives the thermally sensitive benzyl cation [Ti(CH$_2$Ph)(OC$_6$H$_2$-$^tBu_2$-4,6)$_2${S(CH$_2$)$_2$S}]$^+$ upon reaction with B(C$_6$F$_5$)$_3$ in bromobenzene (Scheme 5). At −30 °C two C_1-symmetric diastereomers in a 60:40 ratio are observed, suggesting that epimerization does not

Scheme 4.

Scheme 5.

Table 1
Styrene polymerization with bis(phenolato) complexes activated by methylaluminoxane (except for runs 3 and 4)

Run	Complex	T (°C)	Activity[a]	T_m (°C)	$M_n \times 10^{-4}$	M_w/M_n
1[b]	**2a**	40	1543	223	265.4	2.0
2[b]	**3a**	40	571	223	171.8	1.8
3[c]	**4a**	25	9	202	4.5	1.8
4[c]	**4a**	−20	4	223	4.1	1.2
5[b]	**5a**	50	22	218	16.3	1.9
6[d]	**6a**	50	9	220	4.0	1.9
7[b]	**2b**	40	52	260	0.7	43.5[e]
8[f]	**3b**	50	3	267	n.d.	n.d.

[a] g(polymer)/(mmol catalyst) [styrene mol/l] h.
[b] Polymerization conditions: 1.00×10^{-4} mol of complex; [Al(MAO)]:[M] = 1500; 3.5 mol/l styrene in toluene.
[c] 0.01 mmol Ti; [Ti]:[Al^{i}Bu$_3$]:[B(C$_6$F$_5$)$_3$] = 1:1:0.9; 0.5 ml styrene in 10 ml of toluene.
[d] Polymerization conditions: 1.25×10^{-5} mol of complex; [Al]:[M] = 500; 5 ml of styrene in 15 ml of toluene.
[e] Bimodal.
[f] In 5 ml of toluene.

take place on the NMR time scale at this temperature. The fluxional process at higher temperatures may occur through the helicity change of the tetradentate ligand or site epimerization of the benzyl group. Although it is conceivable that the hemilabile nature of the sulfur coordination results in a transition state with a mirror plane, we favor the possibility that the "swinging" of the benzyl is a facile process.

When polymerization by **2a** was performed in the presence of ^{13}C-enriched $Al(CH_3)_3$, the isolated polymer contained a labeled methyl group due to $CH(Ph)$-$CH_2{}^{13}CH_3$; this suggests that the active species formed from the dichloro complex contains a methyl group at the titanium center as a result of methyl exchange between aluminum and titanium. Moreover, the chemical shift of δ 11.8 ppm in the ^{13}C NMR spectrum of this material indicates that the first insertion into the Ti-${}^{13}CH_3$ bond of the active species must have occurred in a secondary fashion [16]. The absence of any detectable head-to-head or tail-to-tail sequence in the spectrum suggests that the polymerization is highly regiospecific for both the initiation step and the propagation step.

Albeit with significantly lower activity, the 1,4-dithiabutane-bridged complexes of zirconium and hafnium **5a** and **6a** also show isospecific polymerization activity for styrene. This finding suggests the critical importance of a C_2-symmetric ligand sphere for the isospecific styrene polymerization. On the other hand, the low activity of the 1,5-dithiapentane-bridged titanium complexes **2b** and **3b** indicates that the catalytic species is a product of decomposition of the catalyst under the polymerization conditions, as commonly accepted for syndiospecific styrene polymerization [5d]. We suspect that the alkyl cation derived from the longer 1,5-dithiapentane-bridge more readily undergoes reduction by homolytic dissociation of the alkyl radical to give Ti(III) species than the corresponding complex with a 1,4-dithiabutane-bridge [17]. Further investigations into the structure–activity/stereoselectivity relationships revealed that the steric bulk of the *ortho*-substituents at the phenolato group play another critical role. Thus the parent dichloro complex without the bulky *ortho*-substituents $[TiCl_2(OC_6H_4)_2\{S(CH_2)_2S\}]$ were reported to be nonstereorigid and syndiospecific toward styrene upon MAO activation [14c].

3. Conclusion

In conclusion, we have found a new class of easily accessible group 4 complexes such as **2a**–**6a** that are structurally well-characterized single-site catalyst precursors for stereospecific styrene polymerization. Utilizing the rather facile modification of the linked bis(phenolato) ligand sphere, control of stereoselectivity during single-site polymerization of styrene became pos-

sible. Further examples for stereoregulating property of this class of catalyst precursors include 3,4-methylpentadiene [18]. However, the polymerization of simple α-olefins is sluggish and not stereoselective, although copolymerization of propylene with styrene appears to occur [19]. Finally it is worthy noting that the homopolymerization of ethylene gives branched polyethylene [20a], whereas copolymerization with styrene results in alternating ethylene–styrene copolymers [20b].

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