

Review

Non-metallocene catalysts for the styrene polymerization: isospecific group 4 metal bis(phenolate) catalysts

Carmine Capacchione^a, Antonio Proto^a, Henner Ebeling^b, Rolf Mülhaupt^b, Klaus Möller^c, R. Manivannan^c, Thomas P. Spaniol^c, Jun Okuda^{c,*}

^a Dipartimento di Chimica, Università di Salerno, Via S. Allende, I-84081 Baronissi (SA), Italy

^b Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie, Albert-Ludwig-Universität Freiburg, Stefan-Meier-Strasse 21, D-79104 Freiburg, Germany

^c Institut für Anorganische Chemie, Aachen University of Technology (RWTH), Prof.-Pirlet-Strasse 1, D-52056 Aachen, Germany

Abstract

The development of an isospecific styrene polymerization catalysts system based on methylaluminumoxane (MAO)-activated group 4 metal non-metallocene complexes is reported. The ligand derived from the 1,4-dithiabutanediyl-linked bis(phenol)s has been designed in order to ensure stereochemical rigidity utilizing the potentially hemi-labile function of the sulfur donors. Isospecificity during styrene polymerization was achieved using easily accessible catalyst precursors of the type $[MX_2(OC_6H_2-^iBu_{2-4}, 6)_2\{S(CH_2)_2S\}]$ ($M = Ti, Zr, Hf; X = Cl, CH_2Ph$). A remarkable dependence of both the activity and stereoselectivity on the ligand backbone was observed, as analogous precursors with 1,5-dithiapentanediyli-linked bis(phenolato) ligand gave syndiotactic polystyrene with lower activity.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Styrene; Non-metallocene catalyst; Stereoselective polymerization; Titanium; Stereorigidity

1. Introduction

In contrast to the remarkable level of stereocontrol during propylene polymerization through the rational design of metallocene structure [1,2], there have so far been no general ways to influence the stereoselectivity during the polymerization of the commodity monomer styrene [3]. Syndiotactic polystyrene, discovered by Ishihara et al. [4] at Idemitsu, is produced by trivalent mono(cyclopentadienyl)titanium catalysts [5] and has recently been commercialized as a new high melting, fast crystallizing, chemically resistant thermoplastic (Xarec®). The practically perfect syndiotacticity resulting in high crystallinity, however, could not be influenced significantly, 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, but suffers from low crystallization rate [6–8]. Except for a recent

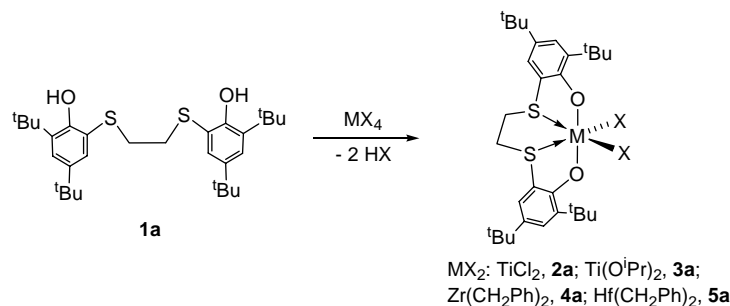
report on isospecific styrene polymerization by C_1 -bridged Brintzinger-type zirconocene by Arai et al. [7], the synthesis of isotactic polystyrene by single-site organometallic catalysts remains virtually unknown. Recently, we discovered a family of structurally well-characterized non-metallocene group 4 metal catalyst precursors [9,10] that efficiently polymerize styrene to give isotactic polystyrene [11].

2. Results and discussion

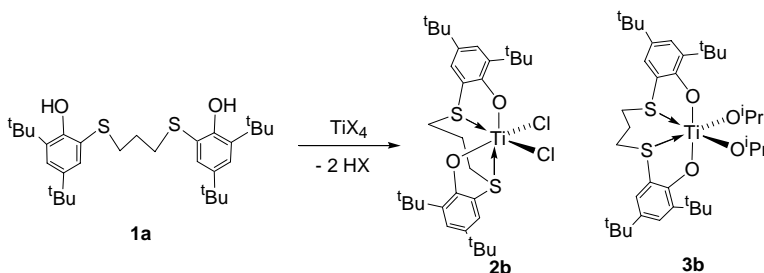
It has been long known that titanium complexes with a 2,2'-sulfur-bridged bis(phenolato) ligand of the type $[Ti\{(OC_6H_2-^iBu_{2-4}, 6)_2S\}_2X_2]$ are active in syndiospecific styrene polymerization upon activation with methylaluminumoxane (MAO) [12]. The report on isospecific living 1-hexene polymerization by a diamine-bis(phenolato) zirconium catalyst as well as other structurally defined stereospecific non-metallocene catalysts [9] intrigued us to develop new styrene polymerization catalysts with controllable stereoregulating property. Thus, we prepared two new bis(phenols), $(HOC_6H_2-^iBu_{2-4}, 6)_2\{S(CH_2)_nS\}$ **1a** ($n = 2$)

* Corresponding author. Tel.: +49-241-8094645; fax: +49-241-8092644.

E-mail address: jun.okuda@ac.rwth-aachen.de (J. Okuda).



Scheme 1.



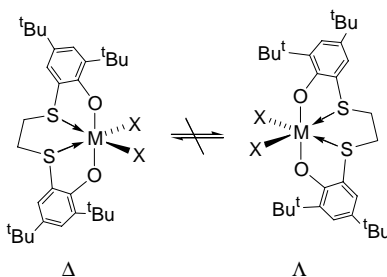
Scheme 2.

and **1b** ($n = 3$), with a $1,\omega$ -dithiaalkanediy bridge, by nucleophilic substitution of the corresponding $1,\omega$ -dibromoalkane by 3,5-di-*tert*-butyl-2-hydroxybenzenethiol [13]. Our initial attempts to obtain stereorigid bis(phenolato) titanium complexes were not successful [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 bisphenol with a 1,5-dithiapentane-link **1b** analogously gave the titanium complexes **2b** and **3b** in quantitative yield. It is noteworthy that these clean complexation reactions are well-suited for automated synthesis (Scheme 2).

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

Crystallographic structure determination of an analogue of **2a** [$\text{TiCl}_2(\text{OC}_6\text{H}_2\text{-}^t\text{Bu-6-Me-4})_2\{\text{S}(\text{CH}_2)_2\text{S}\}$] confirms that this complex adopts a C_2 -symmetrical configuration with *cis*-arranged chloro ($\text{Cl-Ti-Cl } 103.4(1)^\circ$) and thioether groups ($\text{Ti-S1 } 2.647(3)$, $\text{Ti-S2 } 2.647(3)$ Å). Fig. 1 depicts the molecular structure of the Λ configurational isomer.



Scheme 3.

The two sulfur atoms of the link, which shows a *gauche* conformation with dihedral angle SCCS of $54.5(10)^\circ$, evidently enforce the *trans*-coordination of the two bulky phenolato ligand moieties. Without the sulfur coordination,

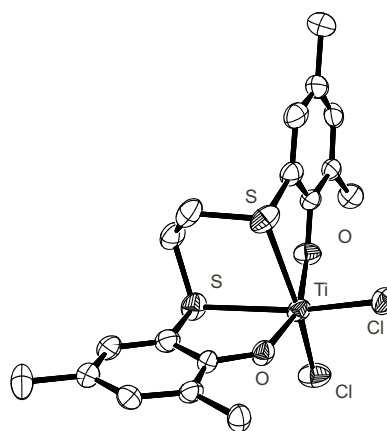


Fig. 1. Molecular structure of the Λ isomer of **2a'**. Methyl groups of the *tert*-butyl groups have been omitted.

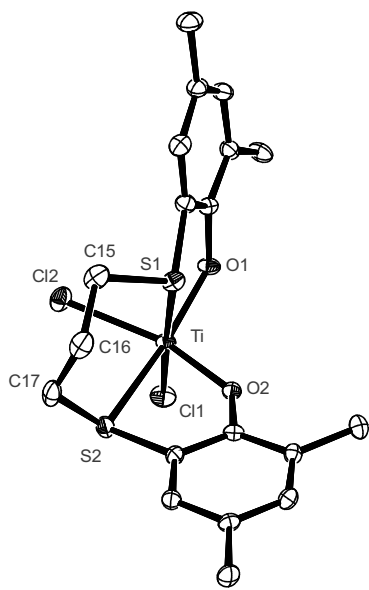


Fig. 2. ORTEP diagram of the molecular structure of **2b**. Methyl groups of the *tert*-butyl groups have been omitted.

the coordination geometry would be tetrahedral and thus non-chiral.

In contrast, **2b** shows at room temperature a pattern of broad signals due to fluxional behavior. The low-temperature ^1H 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**, indicating that for the 1,5-dithiapentane-linked bis(phenolato) complexes stereorrigidity is not observed. The interconversion between C_2 - and C_1 -symmetric configuration can be thought of a flipping of one OTiS chelate ring.

Upon activation with methylaluminoxane, 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 1–8 have isotactic microstructure, whereas the polystyrenes produced in runs 9–11 have syndiotactic microstructure [15]. GPC analysis of the isotactic polymers shows polydispersity indices of about 2, as expected for single-site catalysts.

As active species, we assume an alkyl cation $[\text{TiR}(\text{OC}_6\text{H}_2\text{-}^i\text{Bu}_2\text{-}4,6)_2\{\text{S}(\text{CH}_2)_2\text{S}\}]^+$ in analogy to similar non-metallocene polymerization catalysts [10]. The dichloro titanium complex **2a** can be smoothly converted into the dibenzyl complex $[\text{Ti}(\text{CH}_2\text{Ph})_2(\text{OC}_6\text{H}_2\text{-}^i\text{Bu}_2\text{-}4,6)_2\{\text{S}(\text{CH}_2)_2\text{S}\}]$ which according to NMR spectroscopic analysis gives the

Table 1

Styrene polymerization with bis(phenolato) complexes activated by methylaluminoxane

Run	Catalyst	Yield (g)	Activity ^a	T_m (°C)	$M_n \cdot 10^{-4}$	M_w/M_n
1 ^b	2a	15.50	1543	223	265.4	2.0
2 ^b	3a	11.90	571	223	171.8	1.8
3 ^c	2a	2.00	70	217	34.5	1.7
4 ^d	3a	1.30	24	227	95.8	1.8
5 ^d	4a	1.20	22	218	16.3	1.9
6 ^e	5a	0.50	9	220	4.0	1.9
7 ^{e,e}	5a	0.17	3	208	1.0	2.1
8 ^{e,f}	5a	0.03	0.6	225	4.2	3.0
9 ^b	2b	1.30	52	260	0.7	43.5 ^g
10 ^d	2b	0.16	3	264	n.d.	n.d.
11 ^d	3b	0.15	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; $[\text{Al}] : [\text{M}] = 1500$; 3.5 mol/l styrene in toluene at 40 °C.

^c Polymerization conditions: 1.25×10^{-5} mol of complex; $[\text{Al}] : [\text{M}] = 500$; 5 ml of styrene in 15 ml of toluene at 50 °C.

^d In 5 ml of toluene.

^e At 25 °C.

^f At 0 °C.

^g Bimodal.

thermally sensitive, benzyl cation $[\text{Ti}(\text{CH}_2\text{Ph})(\text{OC}_6\text{H}_2\text{-}^i\text{Bu}_2\text{-}4,6)_2\{\text{S}(\text{CH}_2)_2\text{S}\}]^+$ upon reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene. At -30 °C, two C_1 -symmetric diastereomers in a 60:40 ratio is observed, suggesting that epimerization does not take place on the NMR time scale.

When polymerization by **2a** was performed in the presence of ^{13}C -enriched $\text{Al}(\text{CH}_3)_3$, the isolated polymer contained a labeled methyl group due to $\text{CH}(\text{Ph})\text{CH}_2\text{-}^{13}\text{CH}_3$; 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 $\text{Ti}-^{13}\text{CH}_3$ bond of the active species must have occurred in a secondary fashion [16]. The absence of any detectable head-to-head sequence in the spectrum suggests that the polymerization is highly regiospecific for both the initiation step and the propagation step.

Albeit with lower activity, the 1,4-dithiabutane-bridged complexes of zirconium and hafnium **4a** and **5a** also polymerize styrene isospecifically. This finding indicates that the presence of a C_2 -symmetric ligand sphere is critical for the isospecific styrene polymerization. On the other hand, the low activity of the 1,5-dithiapentane-bridged titanium complexes **2b** and **3b** suggests that the catalytic species is a product of decomposition of the catalyst precursor under the polymerization conditions, as commonly accepted for syndiospecific styrene polymerization [5]. We suspect that the alkyl cation derived from the longer 1,5-dithiapentane-bridge is more prone to reduction by homolytic dissociation of the alkyl radical to give Ti(III) species than the corresponding complex with a 1,4-dithiabutane-bridge [17].

3. Conclusion

In conclusion, we have found a new class of easily accessible, structurally well-characterized group 4 complexes that are single-site catalyst precursors for stereospecific styrene polymerization. Based on the rather facile modification of the ligand sphere, control of stereoselectivity during single-site polymerization of styrene became possible for the first time. Initial experiments also bode well for developing further examples of stereoregulating non-metallocene catalysts for other monomers [18].

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung und Forschung, BASF AG, and the Fonds der Chemischen Industrie for financial support. C.C. was a fellow of the International Max Planck Research School on Polymer Science.

References

- [1] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [2] (a) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* 100 (2000) 1253;
(b) G.W. Coates, *Chem. Rev.* 100 (2000) 1223.
- [3] (a) K.C. Hultsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, *Organometallics* 19 (2000) 228;
(b) J. Okuda, S. Arndt, K. Beckerle, K.C. Hultsch, P.-J. Sinnema, P. Voth, T.P. Spaniol, *J. Mol. Catal.* 190 (2002) 215;
(c) S. Harder, F. Feil, K. Knoll, *Angew. Chem. Int. Ed.* 40 (2001) 4261;
(d) S. Harder, F. Feil, *Organometallics* 21 (2002) 2268.
- [4] (a) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2464;
(b) N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356.
- [5] (a) For reviews on syndiotactic polystyrene, see: R. Po, Cardi, N. *Prog. Polym. Sci.* 21 (1996) 47;
(b) N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, *J. Mol. Catal. A: Chem.* 128 (1998) 167;
(c) C. Pellecchia, A. Grassi, *Top. Catal.* 7 (1999) 125;
(d). For recent works, see: C. Pellecchia, D. Pappalardo, L. Oliva, A. Zambelli, *J. Am. Chem. Soc.* 117 (1995) 6593;
(e) A. Grassi, C. Lamberti, A. Zambelli, I. Mingozzi, *Macromolecules* 30 (1997) 1884;
(f) M.K. Mahanthappa, R.M. Waymouth, *J. Am. Chem. Soc.* 123 (2001) 12093.
- [6] (a) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* 77 (1955) 1708;
(b) G. Natta, P. Corradini, *Makromol. Chem* 16 (1955) 77;
(c) C. Overberger, H. Mark, *J. Polym. Sci.* 35 (1959) 381;
(d) R.J. Kern, H.G. Hurst, W.J. Richard, *J. Polym. Sci.* 45 (1960) 195.
- [7] (a) Isopropylidene-bridged ansa-zirconocene catalysts were reported to produce isotactic polystyrene: T. Arai, T. Ohtsu, S. Suzuki, *Polym. Preprints* 39 (1) (1998) 220;
(b) T. Arai, S. Suzuki, T. Ohtsu, *Olefin Polymerization ACS Symposium Series 749*, American Chemical Society, Washington, DC, 2000, p. 66.
- [8] (a) For nickel-catalyzed isospecific oligomerization, see: J.R. Ascenso, A.R. Dias, P.T. Gomez, C.C. Romao, Q. Pham, D. Neibecker, I. Tkatchenko, *Macromolecules* 22 (1989) 998;
(b) J.R. Ascenso, A.R. Dias, P.T. Gomez, C.C. Romao, I. Tkatchenko, A. Revillon, Q. Pham, *Macromolecules* 29 (1996) 4172;
(c) G.L. Crosetti, C. Bormioli, A. Ripa, A. Giarusso, L. Porri, *Macromol. Rapid Commun.* 18 (1997) 801;
(d) R. Po, N. Cardi, R. Santi, A.M. Romano, C. Zannoni, S. Spera, *J. Polym. Sci. Part A: Polym. Chem.* 36 (1998) 2119;
(e) For anionic polymerization to give isotactic polystyrene, see: L. Cazzaniga, R.E. Cohen, *Macromolecules* 22 (1989) 4125;
(f) T. Makino, T.E. Hogen-Esch, *Macromolecules* 32 (1999) 5712.
- [9] (a) For examples of non-metallocene catalysts in stereoselective polymerization of α -olefins, see: E.Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* 122 (2000) 10706;
(b) J. Saito, M. Mitani, M. Onda, J. Mohri, S. Ishii, Y. Yoshida, T. Nakano, H. Tanaka, T. Matsugi, S.H. Kojoh, N. Kashiwa, T. Fujita, *Macromol. Rapid Commun.* 22 (2001) 1072;
(c) J. Tian, P.D. Hustad, G.W. Coates, *J. Am. Chem. Soc.* 123 (2001) 5134;
(d) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* 124 (2002) 7888;
(e) K.C. Jayaratne, L.J. Sita, *Am. Chem. Soc.* 122 (2000) 958;
(f) R.J. Keaton, K.C. Jayaratne, D.A. Henningsen, L.A. Koterwas, L. Sita, *J. Am. Chem. Soc.* 123 (2001) 6197.
- [10] For a review on non-metallocene catalysts, see: G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428;
V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283.
- [11] C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, T.P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* 123 (2003) 6197.
- [12] (a) T. Miyatake, K. Mizunuma, M. Kakugo, *Macromol. Chem. Macromol. Symp.* 66 (1993) 203;
(b) E. Masoud, J. Okuda, *Macromol. Chem. Phys.* 199 (1998) 543;
(c) F.G. Sernetz, R. Mülhaupt, S. Fokken, J. Okuda, *Macromolecules* 30 (1997) 1562.
- [13] S.D. Pastor, D.Z.J. Denney, *Heterocycl. Chem.* 25 (1988) 681.
- [14] (a) S. Fokken, T.P. Spaniol, J. Okuda, F.G. Sernetz, R. Mülhaupt, *Organometallics* 16 (1997) 4240;
(b) J. Okuda, S. Fokken, T. Kleinhenn, T.P. Spaniol, *Eur. J. Inorg. Chem.* 2000, 1321–1326.
- [15] P. Longo, A. Grassi, L. Oliva, P. Ammendola, *Makromol. Chem.* 196 (1990) 237.
- [16] P. Ammendola, T. Tancredi, A. Zambelli, *Macromolecules* 19 (1986) 307.
- [17] S.L. Borkowsky, N.C. Baenziger, R.F. Jordan, *Organometallics* 12 (1993) 486.
- [18] C. Capacchione, A. Proto, V. Venditto, J. Okuda, The synthesis of isotactic poly(4-methylpentadiene) became also possible using 2a/MAO, *Macromolecules* 36 (2003) 9249.