Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 252 (2008) 2115–2136

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Group 3 and 4 single-site catalysts for stereospecific polymerization of styrene

Anne-Sophie Rodrigues, Evgueni Kirillov, Jean-François Carpentier*

Catalyse et organométalliques, UMR 6226 CNRS-Université de Rennes 1, 35042 Rennes Cedex, France

Received 28 September 2007; accepted 14 December 2007
Available online 23 December 2007

Contents

Abstract

The present review aims at a comprehensive survey of controlled stereospecific styrene polymerization by single-site catalysts to give syndiotactic and isotactic polystyrene. The early transition metals (groups 3 and 4) complexes that were successfully applied as

---

* Corresponding author. Fax: +33 223 236 939.
E-mail address: jean-francois.carpentier@univ-rennes1.fr (J.-F. Carpentier).

doi:10.1016/j.ccr.2007.12.015

catalyst precursors are reviewed. Catalytic performances and mechanistic insights, in particular in the stereoregulation phenomenon, are discussed.

Keywords: Group 4 metals; Lanthanides; Polymerization catalysis; Stereoselectivity; Styrene

1. Introduction

Polystyrene is a widely used commodity polymer that constitutes 8% of the world polymer market, with an actual production of over 18 millions tonnes per year. Styrene can be polymerized by all the known mechanisms, i.e. radical [which actually accounts for >99% of the abovementioned production of *atactic* polystyrene], anionic, cationic and coordination-insertion catalysis.

Parallel to the work done for ethylene and α-olefins, styrene polymerization mediated by transition metals started to develop in 1950s, first with Ziegler-Natta heterogeneous catalysts and continued later on with “single-site” metallocene systems. Such coordination-insertion polymerization of styrene rapidly proved to be the method of choice – and virtually so far the only technique [1] – for controlling precisely the stereoselectivity of the process and the resulting polystyrene tacticity.

As a matter of fact, isotactic polystyrene was discovered in 1955 by Natta using heterogeneous catalysts based on $TiCl_4/AlR_3$ binary systems [2–5]. Other related systems such as $TiCl_3/AlEt_3$ [6] or $TiCl_3$/MAO [7,8] were found effective with isotacticity up to 95%. Efforts have then focused on variations of the catalyst structure to enhance both activity and selectivity. Supported systems $TiCl_4/MgCl_2/AlEt_3$ show rather good performances, especially when activated by a mixture of $PCl_3/AlEt_3/H_2O$ (up to $2.5\,kg\,PS/g_{Ti}$) [9]. Other metal centers have also been tested, such as in the $VCl_3/AlCl_3$ system that gives highly isotactic polystyrene [10], or have been added to the initial system to obtain a synergetic effect as observed with $NdCl_3$-$TiCl_4/MgCl_2/AlR_3$, which gives higher molecular weight polymer with narrower distribution ($M_w \approx 600{,}000$ g/mol and $M_w/M_n \approx 6.5$ for $NdCl_3$-$TiCl_4$ *vs.* $M_w \approx 380{,}000$ g/mol and $M_w/M_n \approx 8.5$ for $TiCl_4$) [11]. In 2002, a new method combining classical Ziegler-Natta catalysts and ultrasound was reported to yield highly isotactic polystyrene (*mmmm* ca. 99%) with very high molecular weight (M_w up to 4,700,000 g/mol) and narrow molecular weight distribution ($M_w/M_n = 1.6$) [12]. Nevertheless, all those *heterogeneous* systems always produce atactic polystyrene along with the isotactic part, and tedious time- and solvent-consuming fractionation procedures are required. Though, till recently, isospecific polymerization of styrene with *discrete homogeneous* catalysts remained undocumented.

On the other hand, as described in details below, highly syndiotactic polystyrene was first synthesized in 1985 by Ishihara at Idemitsu, using homogeneous titanium half-sandwich catalysts. Noteworthy, this type of polymer had never been prepared by heterogeneous catalysis or other technique before, and has attracted considerable attention as a new material.

For all these reasons, efficient “single-site” catalytic systems for stereospecific polymerization of styrene have been highly sought after since the mid 1980s [13–18]. Extensive studies have shown the superiority of early transition metal systems (groups 3 and 4), though interesting performances have been noted too for Ni-based systems. In this review, we present the main types of groups 3 and 4 single-site catalysts that have been developed over the past decades for syndiospecific and isospecific styrene polymerization. A special emphasis is given on recently designed discrete systems, which have demonstrated unique abilities. Structure-activity relationships, origins of the stereocontrol and mechanisms are discussed.

2. Syndiospecific styrene polymerization

2.1. Properties and applications of syndiotactic polystyrene

Due to the syndiotactic configuration of the polymer backbone, syndiotactic polystyrene (sPS) is able to crystallize at a relatively high rate [19] to give a semi-crystalline material that can form well-structured spherulitic morphologies when slowly crystallized [20,21]. Four crystalline forms can be observed: the α and β forms correspond to a planar all-trans zigzag backbone structure while the helical γ and δ forms are usually less observed [22]. As a consequence, the polymer presents a high melting temperature ($T_m = 265$–$275\,°C$) while maintaining a glass transition temperature at $T_g = 100\,°C$ [23]. This high melting temperature represents, however, a major processing problem, which limits the actual uses of sPS.

This polymer is also much less soluble than atactic polystyrene in usual solvents [24]. Thus, fractionation in boiling ketones (acetone or 2-butanone) is a commonly used technique to separate atactic and syndiotactic fractions. The percentage of the recovered insoluble fraction (designated by SY) is often used as an estimation of the catalyst stereospecificity, considering that the obtained polymer is highly syndiotactic PS (*rrrr* > 98%).

The polystyrene tacticity is more accurately determined by ^{13}C NMR spectroscopy, using the phenyl *ipso* carbon and the methylene carbon resonances. The methylene signals show a good resolution over a 5 ppm range ($\delta = 42$–47 ppm) while those for the *ipso* carbon are spread over a 2 ppm range ($\delta = 145$–147 ppm). However, the advantage of a determination according to the *ipso* carbon is that signals can be assigned to sequence that increase in *r* dyads when going from low to high field whereas the methylene signals do not display a simple order. First assignments were made on a pentad or hexad level [25,26] but further studies by Harder could improve it up to a heptad level for the *ipso* carbon (Fig. 1) [27].

The unique combination of heat and chemical resistance (against acids, bases, oils, water and steam) with good electrical properties (low dielectric constant and low dissipation factor) along with a low polymer density ($1.05\,g/cm^3$) makes sPS an

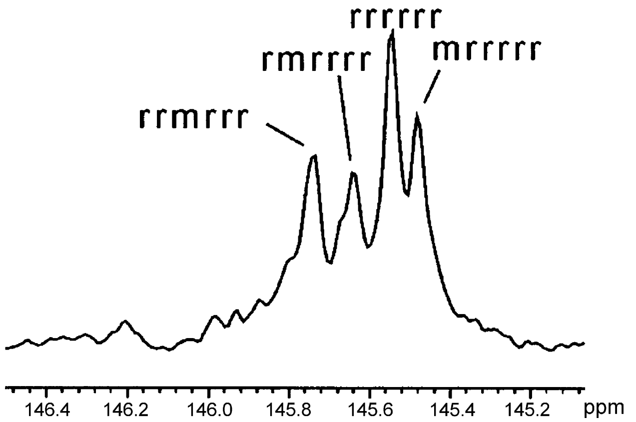


Fig. 1. $^{13}C\{^1H\}$ NMR (150 MHz, 100 °C, TCE-d_2) of *ipso* carbon in syndiotactic-enriched polystyrene (taken from reference [27]).

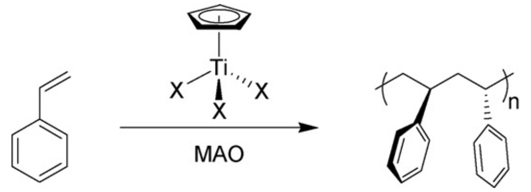
attractive material for applications in automotive (e.g. in the power distribution center under the hood), electrical and electronics (connectors, plugs and sockets), as well as industrial and consumer uses (iron skirts, door internal frame of washing machines and dryers) and food and water contact applications (baking pans or trays that offer a faster and less energy consuming baking process without greasing) [28]. However, these valuable properties are plagued by the high brittleness of sPS.

2.2. Titanium-based catalysts

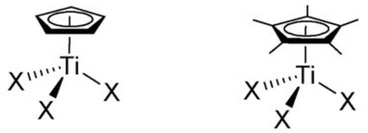
2.2.1. Titanium half-sandwich complexes

The first systems developed for the synthesis of sPS were MAO-activated half-metallocenes of the type $Cp'MX_n$ (Cp' = substituted or unsubstituted, X = halogen, alkoxy or alkyl, $n = 2, 3$; Scheme 1) [29–34]. Remarkably, titanium-based catalysts showed higher activities (and stereospecificities as well) compared with the zirconium ones. This is in striking contrast with previous observations for the reactivity order with other α-olefins. Possible explanations invoked the less electrophilic character of Zr (i.e. softer Lewis acidity), the more difficult reducibility of Zr^{IV} to Zr^{III} (*vide infra*) and a larger ionic radius that would relieve the interactions between the incoming monomer and the growing chain.

Subsequently, a large number of Ti compounds in different oxidation states were more or less successfully used in combination with MAO as polymerization catalysts to afford sPS. Although TiX_4 derivatives (X = Cl, Br, OMe, OEt, O*i*Pr, OBu, Bz) can give sPS (*rr* > 98% for $TiBz_4$), their activities (10–20 kg sPS/(mol$_{Ti}$ h)) are much lower than those of titanium half-sandwich complexes aforementioned (1000–3000 kg sPS/(mol$_{Ti}$ h)) [35–37]. Bis(cyclopentadienyl) compounds and *ansa*-titanocenes give very low yield and/or atactic polymers as well [38].



Scheme 1. Syndiospecific styrene polymerization by titanium half-sandwich complexes [29–34].



1-3 X = Cl, OBu, F **4-6** X = Cl, O*i*Pr, F

Fig. 2. Titanium half-sandwich catalysts precursors used for syndiospecific styrene polymerization [29–34,39,40].

In the $Cp'TiX_3$ series (Fig. 2), fluorides **3** and **6** are the most active [39], followed by alkoxides **2** and **5** [33,40] and chlorides **1** and **4** [39]. This order was attributed to the Ti–X bond polarization (higher in the case X = F) that better allows the formation of a stable active species upon reaction with MAO. A glance at Table 1 shows that Cp^* derivatives ($Cp^* = C_5Me_5$) give a higher degree of syndiospecificity along with higher molecular weights. This has been proposed to stem from a better stabilization of the active center by Cp^*, which is a strong electron donor. As a result, β-H elimination would be retarded and hence the obtained polymers present higher molecular weight.

Recently, some modified half-sandwich Ti complexes (Fig. 3) were reported to show enhanced catalytic performances, i.e. activity and/or syndiospecificity and/or higher molecular weights.

Among those examples are dinuclear Ti half-sandwich complexes bridged by biphenylene (**7–8**), xylene (**9–11**) or hexyl groups (**12–13**) [41,42], or Ti half-sandwich complexes where one of the chloride was replaced by another anionic ligand: aryloxo (**14–25**) [43–46], amide (**26**) [45], anilide (**27**) [45], ketimide (**28–30**) [47] or bidentate aniline-ethoxy (**31–34**) ligand [48]. The improved syndiospecific styrene polymerization abilities of those catalysts (generated upon MAO-activation) are thought to come from cooperative effects between the two active metal centers for the dinuclear complexes. In the case where chloride was replaced by another σ-donor ligand, the latter is assumed to play an important role in stabilizing the active species by partially delocalizing the positive charge of the Ti^{III+} center. Steric factors also have an influence as demonstrated by the different activities observed when varying substituents in aryloxo complexes **14–24**.

2.2.2. Indenyl–Ti complexes

As with Cp^*, replacing the cyclopentadienyl ligand by an indenyl one that has a better electron-donating ability resulted in improved activity, stereospecificity and thermal stability of the catalyst (**35**, Fig. 4) [49]. Further studies focused on the influence of indenyl substituents that was systematically scrutinized through complexes **36–51** [50–53]; complexes with sterically bulky annelated-rings were also reported (**58–63**) [54–56].

These studies led to the conclusions that electron-donating alkyl groups on the indenyl ligand enhanced both the activity and the syndiospecificity of the electrophilic metal center but an increase in the substituents bulkiness (**35–40**) or the presence of a Lewis base (**41**) resulted in an activity and selectivity drop

Table 1
Styrene polymerization performances of some Ti complexes

Complex	MAO/Ti	Temperature (°C)	Time (min)	Activity[a]	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	SY[b] (%)	T_m (°C)	Reference
1	300	50	nr	1,100	140	1.9	nr	258	[39]
2	1,000	45	30	1,589	40	nr	93	258	[33]
3	300	50	nr	3,000	100	2.0	nr	265	[39]
4	300	50	nr	15	169	3.6	nr	275	[39]
5	500	70	30	571	340	nr	>95	270	[40]
6	300	50	nr	690	660	2.0	nr	275	[39]
35	2,000	50	10	6,568	720	nr	98	271	[50]
36	2,000	50	10	7,482	650	nr	94	272	[50]
37	2,000	50	10	3,958	430	nr	92	272	[50]
38	2,000	50	10	422	95	nr	90	271	[50]
51	4,000	50	30	83	nr	nr	95	272	[52]
59	4,000	50	10–30	7,830	424	nr	93	275	[54]
63	4,000	75	10–20	32,600	130	nr	92	265	[55]
64	2,000	25	nr	10	nr	nr	95	272	[60]
65	2,000	25	nr	19	nr	nr	94	272	[60]
66	2,000	25	nr	16	nr	nr	93	273	[60]
67	2,000	25	nr	10	nr	nr	95	273	[60]
68	2,000	20	90	20	nr	nr	84	nr	[61]
69	200	50	60	2	190	4.9	nr	nr	[63]
70	200	20	nr	470	15	nr	>99	270	[64]
71	150	80	120	2,300	46	3.2	>95	268	[65]
72	150	80	120	7,000	19	2.5	> 95	256	[65]
75	150	80	120	32,700	20	2.0	>95	268	[65]
78	150	80	120	111,300	19	3.2	>95	268	[65]
80	1,500	40	120	14	70	2.9	nr	268	[69]
86	1,000	70	10	1,230	292	4.1	98	273	[71]
91	1,000	70	10	683	31	1.8	99	274	[71]
94	1,000	70	10	800	32	1.8	99	275	[71]
97	1,000	70	10	283	136	2.8	97	274	[71]
98	1,000	70	10	1,087	180	1.9	98	273	[72]
98	1,000	30	10	457	872	1.9	99	277	[72]

[a] In kg PS/(mol_{Ti} h).

[b] Percentage of insoluble fraction in refluxing 2-butanone. nr.: not reported.

[50]. Aryl substitution proved to be efficient to enhance both activity and selectivity, as well as polymer molecular weights (M_n up to 1,300,000 g/mol with **57**/MAO) [53].

Annelated-ring complexes also showed improved thermal stability and thus better catalytic performances along with syndiospecificity. High molecular weight polymers could be obtained with those systems (M_w up to 545,000 g/mol with **58**/MAO) [54]. Selected polymerization activities are reported in Table 1.

Fluorinated analogues of complexes **35–42** were also reported and, similarly to Cp derivatives, an improved activity and syndiospecificity, as well as higher molecular weights, were obtained [57]. The influence of the substituents was found to be similar, i.e. only the strong electron-donating and less bulky substituents are beneficial and lead to an increase in the propagation rate without increasing the chain-termination rate by β-H abstraction. An increase in the steric constraints most likely interferes with styrene coordination, thus reducing activity and stereocontrol.

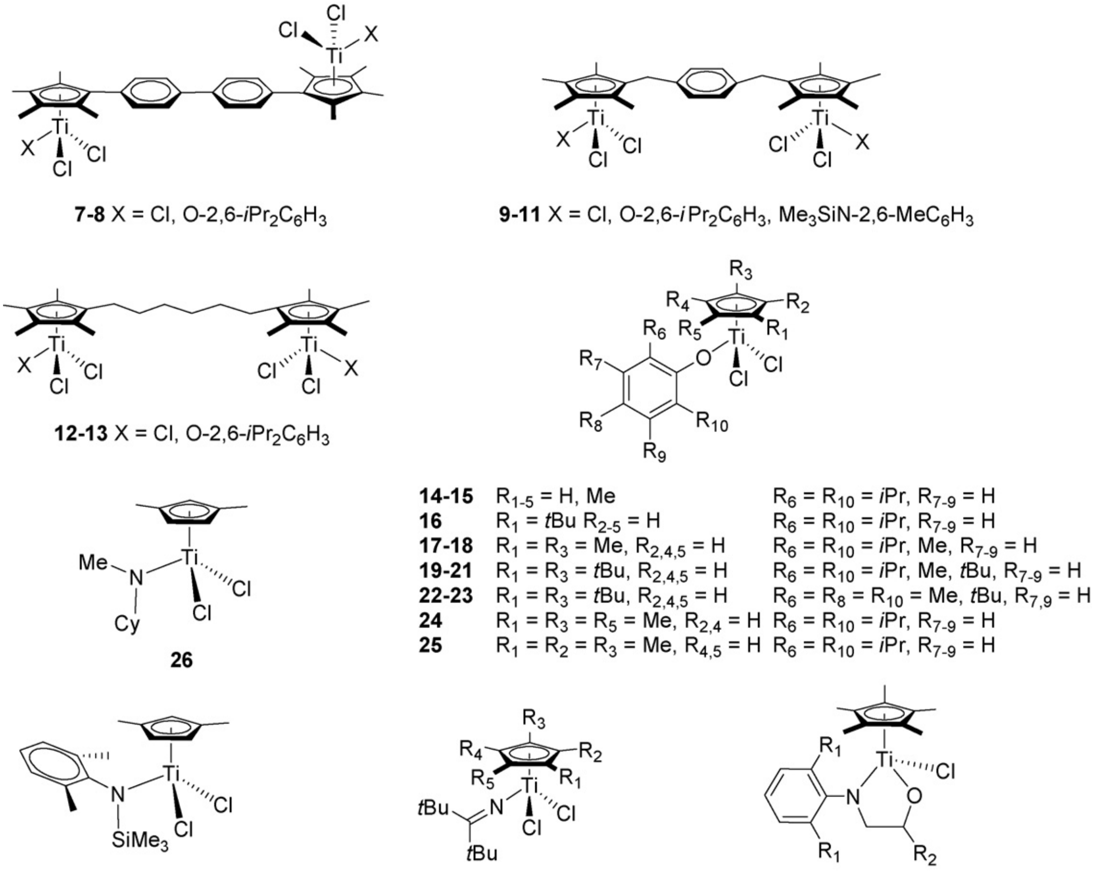
2.2.3. Amidinate–Ti complexes

The bidentate amidinate-type ligand has been considered as a steric equivalent of the ubiquitous cyclopentadienyl ligand and was reported as a promising alternative [58,59]. In this line, Rausch and co-workers [60,61], Zambelli and co-workers [62,63] and Eisen and co-workers [64] synthesized complexes **64–70** (Fig. 5) and reported them to be active pre-catalysts (although with a rather low activity) for the syndiospecific polymerization of styrene.

In the *N*,*N*′-bis(trimethylsilyl)benzamidinate series, the order of activity was found to be **65** > **66** > **64** > **67** (see Table 1). This was explained by the better thermal stability of dimeric **65** compared to **64** that could convert under mild conditions to benzonitrile and $\{(SiMe_3)_2N\}Ti(O\mathit{i}Pr)_3$, which is completely inactive. Expectedly, the coordination of electron-donating ligands (THF, PMe_3) to the metal center also decreases the activity [60]. The system derived from *N*,*N*′-dimethyl-*p*-toluamidinato complex **68** showed lower stereospecificity that was explained by the smaller bulkiness of the *N*-methyl substituents compared to the *N*-trimethylsilyl. The latter group could hence operate a better stereochemical control [61]. This hypothesis was confirmed by the results obtained with the sterically crowded chiral benzamidinate complex **70** that produced highly syndiotactic polystyrene (*rrrr* > 99%) [64].

2.2.4. Bis(phenolate)–Ti complexes

In further efforts to move away from Cp derivatives and thus diversify the ligand scope, Okuda and Masoud reported



7-8 X = Cl, O-2,6-$iPr_2C_6H_3$

9-11 X = Cl, O-2,6-$iPr_2C_6H_3$, Me_3SiN-2,6-MeC_6H_3

12-13 X = Cl, O-2,6-$iPr_2C_6H_3$

14-15 R_{1-5} = H, Me $R_6 = R_{10}$ = *i*Pr, R_{7-9} = H
16 R_1 = *t*Bu R_{2-5} = H $R_6 = R_{10}$ = *i*Pr, R_{7-9} = H
17-18 $R_1 = R_3$ = Me, $R_{2,4,5}$ = H $R_6 = R_{10}$ = *i*Pr, Me, R_{7-9} = H
19-21 $R_1 = R_3$ = *t*Bu, $R_{2,4,5}$ = H $R_6 = R_{10}$ = *i*Pr, Me, *t*Bu, R_{7-9} = H
22-23 $R_1 = R_3$ = *t*Bu, $R_{2,4,5}$ = H $R_6 = R_8 = R_{10}$ = Me, *t*Bu, $R_{7,9}$ = H
24 $R_1 = R_3 = R_5$ = Me, $R_{2,4}$ = H $R_6 = R_{10}$ = *i*Pr, R_{7-9} = H
25 $R_1 = R_2 = R_3$ = Me, $R_{4,5}$ = H $R_6 = R_{10}$ = *i*Pr, R_{7-9} = H

26

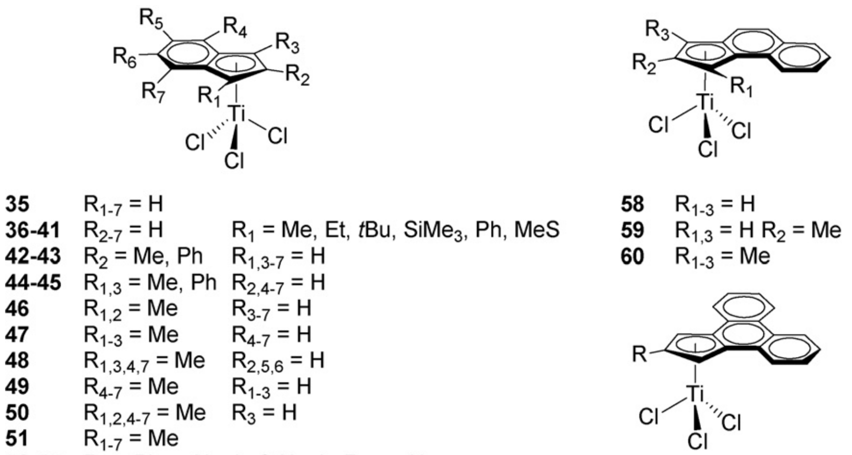
27

28-29 R_{1-5} = H, Me
30 R_1 = *t*Bu R_{2-5} = H

31-34 R_1 = H, Me R_2 = H, Me

Fig. 3. Modified Ti half-sandwich catalyst precursors used for syndiospecific styrene polymerization [41–48].

complexes **71–85** incorporating bis(phenolate) ligand (Fig. 6) to promote the syndiospecific polymerization of styrene with an outstanding high activity (Table 1) [65–69]. Both the nature of the Z linker in the bis(phenolato) ligand and the ancillary ligand X appeared to influence the polymerization activity. For the same set of X ligand (X = Cl), the activity followed the order: Z = CH_2=CH_2–CH_2 ≪ S = O=S (Table 1). This effect was ascribed to the increase of the Lewis acidity due to the presence of sulfur [65]. An enhanced stability of the active species due to [weak] sulfur coordi-

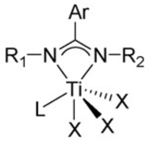


35 R_{1-7} = H
36-41 R_{2-7} = H R_1 = Me, Et, *t*Bu, $SiMe_3$, Ph, MeS
42-43 R_2 = Me, Ph $R_{1,3-7}$ = H
44-45 $R_{1,3}$ = Me, Ph $R_{2,4-7}$ = H
46 $R_{1,2}$ = Me R_{3-7} = H
47 R_{1-3} = Me R_{4-7} = H
48 $R_{1,3,4,7}$ = Me $R_{2,5,6}$ = H
49 R_{4-7} = Me R_{1-3} = H
50 $R_{1,2,4-7}$ = Me R_3 = H
51 R_{1-7} = Me
52-54 R_1 = Ph, α-Naph, β-Naph R_{2-7} = H
55-57 R_2 = Ph, α-Naph, β-Naph $R_{1,3-7}$ = H

58 R_{1-3} = H
59 $R_{1,3}$ = H R_2 = Me
60 R_{1-3} = Me

61-63 R = H, Me, Ph

Fig. 4. Indenyl Ti catalyst precursors used for syndiospecific styrene polymerization [49–56].



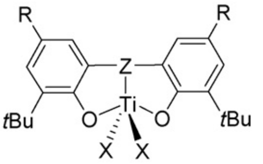
64-65	Ar = Ph	X = O*i*Pr, Cl	L = none	$R_1 = R_2 = \mathrm{SiMe}_3$
66-67	Ar = Ph	X = Cl	L = THF, PMe_3	$R_1 = R_2 = \mathrm{SiMe}_3$
68	Ar = Tol	X = Cl	L = THF	$R_1 = R_2 = \mathrm{Me}$
69	Ar = Bz	X = Cl	L = none	$R_1 = R_2 = i\mathrm{Pr}$
70	Ar = Ph	X = Cl	L = THF	$R_1 = \mathrm{SiMe}_3$ R_2 = myrtanyl

Fig. 5. Amidinate-Ti catalyst precursors used for syndiospecific styrene polymerization [60–64].

nation might be envisioned as well. The additional X ligand also exerts a strong influence: in fact, broad polydispersities ($M_w/M_n = 4.8$–13.7) were observed when X = O*i*Pr, while the best activities (178,000–380,000 kg sPS/($\mathrm{mol_{Ti}}$ h) for **74** and **77**) were observed with X = Cp*. In this latter case, this might come from the formation of $[\mathrm{Cp^*Ti^{III}R}]^+$ species, which is thought to be the active species for syndiospecific styrene polymerization catalyzed by half-titanocene complexes (*vide infra*). Overall, high molecular weight polystyrenes are obtained with $M_w/M_n \approx 2$, indicative of a single-site polymerization. It should also be noted that only a very low amount of MAO (Al/Ti = 150) was used compared to the previous systems [65]. When a 1,5-dithiapentanediyl bridge was used (**80–85**), low activities were observed, independently on the X ligand and the R substituents [69].

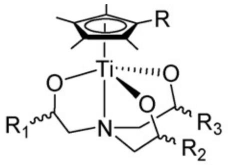
2.2.5. Titanatrane complexes

More recently, Do and co-workers described a series of new half-titanocenes incorporating triethanolatoamine ligands (Fig. 7) that, upon activation with MAO, showed moderate to high activity for syndiospecific styrene polymerization [70–72]. The substituents influence of the Cp and triethanolatoamine ligands was systematically investigated. The best catalytic performances were obtained when R = Me and the steric effects of R_1, R_2 and R_3 were found to be determining factors for the activity. The activity order was: **86** > **94** > **91** ≈ **92** ≈ **95** > **96** ≈ **93** > **97**. Highly syndiotactic polymers (SY > 97%) with moderate to high molecular weights (M_w = 31,400–292,000 g/mol) and narrow distributions (M_w/M_n = 1.8–2.7) were obtained, except for **86** that gave M_w/M_n = 4.1 [71].



71	Z = $\mathrm{CH_2}$	X = Cl	R = Me
72-74	Z = $\mathrm{CH_2CH_2}$	X = Cl, O*i*Pr, Cp*	R = Me
75-77	Z = S	X = Cl, O*i*Pr, Cp*	R = Me
78-79	Z = S=O	X = Cl, O*i*Pr	R = Me
80-85	Z = $\mathrm{S(CH_2)_3S}$	X = Cl, O*i*Pr	R = Me, *t*Bu, OMe

Fig. 6. Bis(phenolate) Ti catalyst precursors used for syndiospecific styrene polymerization [65–69].



86-90	$R_1 = R_2 = R_3$ = H	R = Me, H, Et, Ph, Tol
91	$R_1 = R_2 = R_3$ = (*S*)-Me	R = Me
92	$R_1 = R_3$ = (*S*)-Me R_2 = H	R = Me
93	R_1 = (*S*)-Me $R_2 = R_3$ = H	R = Me
94	$R_1 = R_2 = R_3$ = (*R*)-Me	R = Me
95	$R_1 = R_3$ = (*R*)-Me R_2 = H	R = Me
96	R_1 = (*R*)-Me $R_2 = R_3$ = H	R = Me
97	$R_1 = R_2 = R_3$ = Me	R = Me
98	$R_1 = R_2 = R_3$ = (*R*)-Ph	R = Me

Fig. 7. Titanatrane catalyst precursors used for syndiospecific styrene polymerization [70–72].

In a further contribution, the influence of polymerization conditions was examined and performances of the previous complexes were compared with those of complex **98** [72]. The latter complex, upon activation with MAO, was found to give very high molecular weight sPS (M_w = 180,000–870,000 g/mol). This increase in the molecular weight was attributed to the steric bulkiness and electronic effects of the phenyl substituents, which make the termination processes such as β-H elimination or chain transfer reaction by $\mathrm{AlMe_3}$ less affordable. As expected, activities for all complexes increased with increasing polymerization temperature but this led to a slight decrease in molecular weights [72].

2.2.6. Overview

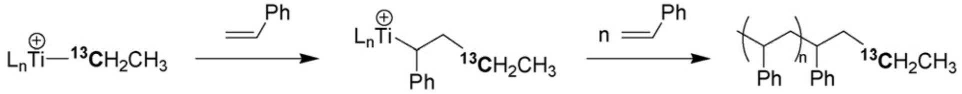
The catalytic performances of the abovementioned complexes are summarized and compared in Table 1. The order of activity for the different types of catalysts is the following: benzamidinate < titanatrane < half-sandwich complexes < bis(indenyl) < bis(phenolate). This trend denotes a subtle equilibrium between the steric bulkiness around the metal center and the necessary electron density provided by the ligand to achieve both high activity and selectivity. However, it should be kept in mind that different polymerization conditions (MAO/Ti ratio, activation temperature and time, polymerization temperature and time, solvent, etc.) were used, which might complicate the direct comparison of these activity data.

2.3. Polymerization mechanism

A considerable amount of research has been directed towards the comprehension of syndiospecific styrene polymerization mechanism. The nature of the true active species is not yet fully elucidated and continues to be the matter of extensive studies.

2.3.1. Active species

Pioneering investigations by electron spin resonance (ESR) were carried out by Chien et al. to determine the oxidation state of the active species [34]. Mainly $\mathrm{Ti^{III}}$ species were observed [73–76] but further studies have also implicated $\mathrm{Ti^{II}}$ [36,76,77]



Scheme 2. Determination by ^{13}C labelling study of the regiochemistry in the initiation step of syndiospecific styrene polymerization.

and Ti^{IV} [74,76] species, as well as mixtures of species in various oxidation state. Recently, Waymouth ruled out the hypothesis of a Ti^{IV} active species for a syndiospecific styrene polymerization performed in the dark [78]: as a matter of fact, the Ti^{IV} precursor Cp*TiBz$_3$ activated by [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] gave, in the dark, only traces of atactic PS; on the other hand, when styrene polymerization was performed with the latter combination in the presence of natural light or with the combination of the Ti^{III} species Cp*Ti(C$_3$H$_5$)$_2$/[PhNHMe$_2$][B(C$_6$F$_5$)$_4$] used in the dark, sPS was obtained in good yield. These observations indicate a similar catalytically active species and suggest that the Ti^{IV} species undergoes reduction to Ti^{III} when exposed to light [78].

Moreover, NMR monitoring of the stoichiometric reaction between Cp*TiR$_3$ with B(C$_6$F$_5$)$_3$ showed the formation of the expected Ti^{IV} product [Cp*TiR$_2$]$^+$[RB(C$_6$F$_5$)$_3$]$^-$ but this complex was found to decompose to Ti^{III} species under polymerization conditions [79,80].

Consequently, it is now generally admitted that the active species is a cationic Ti^{III} complex of the type [CpTiR]$^+$ formed in three steps: (1) alkylation by MAO or AlR$_3$, (2) cationization by ligand abstraction and (3) reduction of Ti^{IV} to Ti^{III}; though, the exact order of those steps is still unclear.

2.3.2. Regio- and stereochemistry

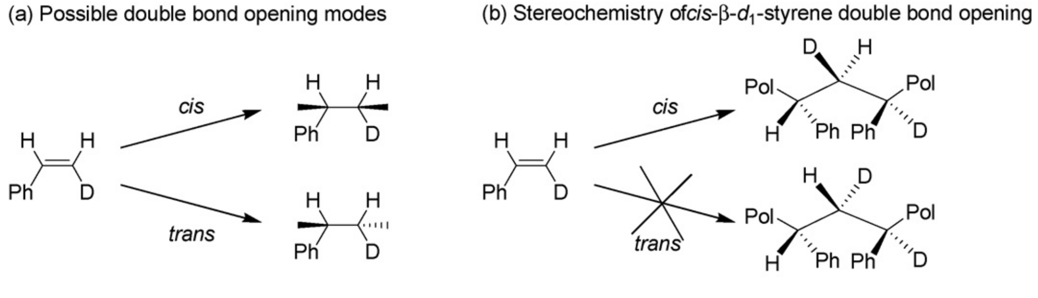
The regiochemistry of Ti-catalyzed styrene polymerization was elegantly determined by NMR analyses of ^{13}C-enriched samples prepared with the catalytic system TiBz$_4$/MAO/Al(^{13}CH$_2$CH$_3$)$_3$. Those polymers showed the presence of –CH(Ph)CH$_2$^{13}CH$_2$CH$_3$ end-groups that unambiguously indicate a secondary insertion of the monomer in the initiation step (Scheme 2) [81]. An equal amount of saturated CH$_3$(Ph)CH– and unsaturated PhCH=CH– end-groups detected on low molecular weight sPS along with the lack of detectable regio-inversions (head-to-head and tail-to-tail sequences) demonstrate that the regiochemistry of styrene insertion is also secondary in the propagation steps [82]. This regiochemistry is opposite to that generally involved in α-olefins polymerization with metallocene catalysts but it should be noted that, due to its aromatic character and electronic polarization, styrene cannot be considered as a “classical” α-olefin.

There are two possibilities for the addition mode of the growing polymer chain to the styrene double bond: by *cis*- or *trans*-opening of the double bond (Scheme 3a). In the case of propylene Ziegler-Natta polymerization, it is known that polymerization occurs by *cis*-opening of the double bond [83]. Longo determined by copolymerizing perdeuteriostyrene with *cis*-β-*d*$_1$-styrene and analyzing the coupling constants that styrene insertion also proceeds by *cis*-opening of the double bond: since most of the *d*$_1$-styrene units are surrounded by perdeuteriostyrene units, the methylene protons are coupled only with one methine proton. The observed coupling constant was $J = 9.0$ Hz, which is assigned to a *trans* geometry, the value assigned for *cis* geometry being lower ($J = 5.4$ Hz). Thus, it was concluded that polymerization takes place through *cis*-addition of the growing polymer chain to the monomer double bond (Scheme 3b) [84].

2.3.3. Stereocontrol mechanism

The stereochemical composition of sPS samples prepared with CpTiCl$_3$/MAO was determined by ^{13}C NMR spectroscopy and was found in good agreement with the Bernoullian statistical model. The polymer microstructure can be described as long sequences of *racemic* diads with only isolated *meso* diads. This type of microstructure is expected for a chain-end controlled mechanism, the steric control arising from a 1,3-*unlike* asymmetric induction from the last inserted monomer unit to the incoming monomer unit. In other words, the syndiotactic configuration results from the phenyl–phenyl repulsive interaction (Scheme 4) [85].

Zambelli initially suggested an η^4-coordination of styrene and an η^3-coordination of the last styrene unit of the growing polymer chain (Pol) in the cation [CpTi^{III}(Pol)(styrene)]$^+$; for non-cyclopentadienyl complexes, a replacement of the anionic Cp ligand by a neutral η^6-arene ligand (toluene or styrene) was proposed [32,86]. However, it seems now more reasonable to envision an η^2-styrene coordination and an η^n ($n \geq 3$) benzyl coordination of the last inserted monomer unit of the grow-



Scheme 3. Stereochemistry of styrene double bond opening (Pol = polymer chain) [84].

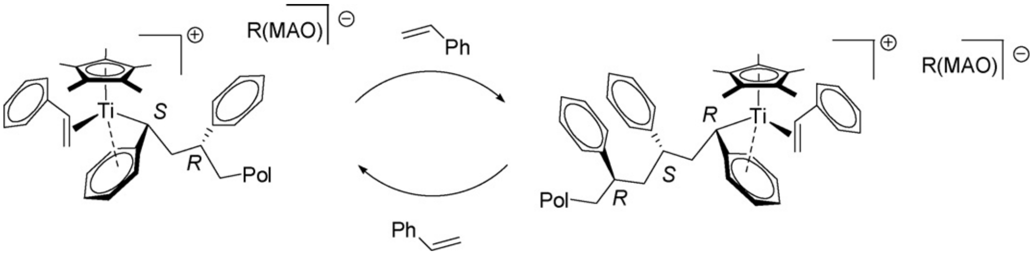
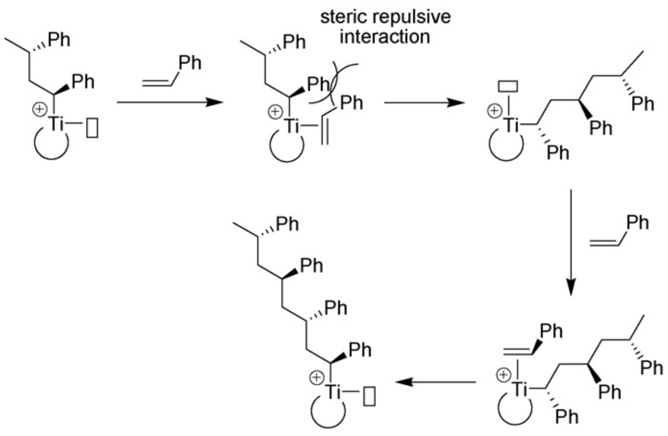


Fig. 8. Proposed propagation active site (Pol = polymer chain).



Scheme 4. Steric control of syndiospecific propagation [85].

ing polymer chain (Fig. 8). This last assumption was supported by ESR results suggesting a partial delocalization of the Ti^{III} nucleus d^1 electron on the aromatic ring of the last styrene unit in the growing chain [16,75]. This interaction most probably provides further stereochemical control as suggested in Fig. 8.

A carbocationic polymerization mechanism was also proposed by Baird and co-workers for the $Cp^*TiMe_3/B(C_6F_5)_3$ system [87]. They indeed observed the formation of $[Cp^*TiMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ in aromatic solvents and since the arene ligand is readily displaced, they hypothesized that $[Cp^*TiMe_2]^+$ could behave as an initiator for carbocationic polymerization. As evidences, they assigned NMR resonances to alkoxy end-groups for samples quenched with alcohols; however, these proved later to have been mistakenly assigned. The stereocontrol was initially attributed to the strong ion pairing of $MeB(C_6F_5)^-$ counterion with the cationic center [87]. Nevertheless, those results were refuted and further evidences for polyinsertion were given [88]. A real carbocationic styrene polymerization with this system was found later possible, but only at temperatures below −15 °C, giving atactic PS. Thus, the authors retracted their earlier conclusion that sPS is formed *via* a carbocationic mechanism [89,90].

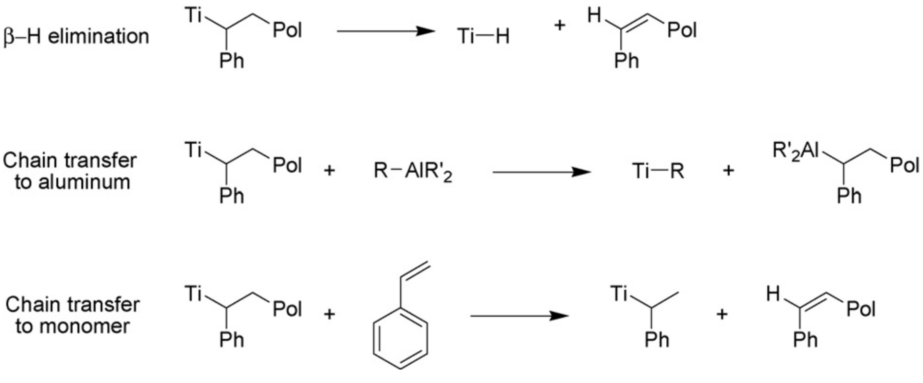
2.3.4. *Termination reactions*

Polymerization termination occurs predominantly by β-H elimination and chain transfer to the aluminum co-catalyst [82,91], although transfer to the monomer has also been observed [33] (Scheme 5). The β-H elimination seems to be predominant for syndiospecific styrene polymerization rather than for ethylene polymerization by metallocenes because of a smaller activation barrier [92].

2.3.5. *Co-catalyst and counterion role*

As for metallocene catalysis, MAO is the most commonly used co-catalyst for syndiospecific styrene polymerization. It acts as a weak reducing and an alkylating agent of the transition metal center. It has to be used in a large excess (molar ratio Al/Ti from 100 to 5000) and the amount of residual trimethylaluminum (TMA) has a significant influence on the catalytic performances. Thus, an increase in TMA amounts led to a significant decrease in activity and polymer molecular weight, due to competitive coordination to the metal center and chain transfer, respectively [93,94]. The molecular weight of MAO also apparently affects the polymerization activity: with increasing MAO molecular weight, the catalyst activity increases and reaches a good performance at molecular weight of ca. 500 g/mol [95].

In addition to MAO, boranes such as $B(C_6F_5)_3$ and its derivatives can be used as co-catalysts of alkyl- and benzyl–metal



Scheme 5. Termination pathways of syndiospecific styrene polymerization.

complexes and are already active in an equimolar amount [87,96]. With Cp^*TiMe_3 as the pre-catalyst, the observed polymerization activity upon activation with $[HNMe_2Ph][B(C_6F_5)_4]$ was lower than with $B(C_6F_5)_3$, possibly because of free amine coordination to the active site that interferes with monomer coordination and propagation [96]. Combination of $B(C_6F_5)_3$ and small amounts of AlR_3, e.g. $Al(iBu)_3$ (TIBA), which acts as an impurities scavenger, was found to improve both activity and syndiotacticity of the PS [97].

The role of the counterion has been often neglected and only a few studies reported its influence on tacticity or polymer molecular weight. Polymers with the highest molecular weights were obtained with the $[Ph_3C][B(C_6F_5)_4]$-activated catalysts, i.e. with the less coordinating anion, while MAO-activated systems where the anion could be more strongly coordinated yielded lower average molecular weight sPS products [98]. Even if the role of the co-catalyst is to act as a Lewis acid, that is, to create and maintain the necessary coordinative unsaturation and electron deficiency at the metal center, not all Lewis acids are effective co-catalysts. For instance, BCl_3, BF_3, PF_5, SbF_5, Me_3SnCl, and Me_3SiCl are not suitable candidates, mostly because the halide atoms can either strongly coordinate or irreversibly transfer to the Ti cation [80]. In summary, as in olefin polymerization, both the nature and the ion-pair interactions are crucial to devise efficient co-catalysts.

2.3.6. *Theoretical studies*

It has been shown in the previous sections that many characteristics of the syndiospecific styrene polymerization mechanism have been unambiguously addressed (*cis*-opening of the double bond [84], secondary insertion [81,82], chain-end controlled mechanism [85]), although there still is some debate about the exact nature of the active species. Surprisingly enough, and in sharp contrast to the considerable amount of high level computational studies that have contributed to the detailed comprehension of olefins polymerization with both early [99–122] and late transition metals [123–133], only little has been done on a theoretical point of view in the case of styrene polymerization [134–138]. These computational studies have been essentially intended to rationalize the regio- and stereocontrol observed in the propagation step.

The results for the $[CpTi(Pol)]^+$ model (Pol = growing polystyryl chain) support the supposed η^n-coordination scheme of the last inserted monomeric unit, either with an η^3-coordination presenting a strong σ-bond between the Ti atom and the benzylic carbon atom or an η^7-coordination with all the C atoms of the inserted monomer unit involved [134]. In the latter case, the next styrene unit coordinates in an η^2 fashion while for η^3-coordination of the last inserted monomer unit, the next styrene unit is η^4-coordinated. All these coordination intermediates are of quite similar energy and are separated by low energy barriers. On the other hand, neutral d^2 species of the type $CpTi^{II}(Pol)$ exhibit higher energy barriers and are, therefore, thought unlikely to promote styrene polymerization [134]. The transition state leading to a syndiotactic diad was found to be favored by 6 kJ/mol compared to the transition state leading to an isotactic diad. This is due to steric effects dictated by the Cp ligand. Thus, because of increased repulsive interactions between the benzyl-type growing chain and the bulkier Cp^* or η^6-arene ligands and in agreement with experimental observations, those complexes were calculated to be more stereoselective since the transition states leading to a syndiotactic diad are favored by 16 and 13 kJ/mol, respectively, compared to the transition states leading to an isotactic diad [135].

Ti^{IV} models were also investigated and the results found for the *ansa*-metallocene model $H_2SiCp_2Ti^+\text{-}CH_3$ suggest that primary insertion is favored in the initiation step but lead to a stable product that blocks additional primary insertions [138]. In the propagation step, consistent with the experimental observations, secondary insertion was found to be more favorable due to repulsive interactions between the two phenyl rings of the last inserted styrene and the incoming unit.

2.4. *Group 3 catalysts*

Styrene polymerization by group 3 complexes has been much less explored than Ti-based complex chemistry. Until quite recently, only a few examples of lanthanide-based systems were reported to polymerize styrene (mostly with a rather poor activity) and even a few less to do so in a stereospecific way.

2.4.1. *Early works*

The first example of styrene polymerization initiated by lanthanide catalyst was reported in 1986 by Sen who suggested a cationic mechanism using $[Eu(CH_3CN)(BF_4)_3]_x$ that yielded low molecular weight atactic PS (M_w = 1900–13,000 g/mol) [139]. Sluggish styrene polymerization was also observed with discrete complexes $[(tBuC_5H_4)_2LnMe]_2$ (Ln = Pr, Nd, Gd) [140], $[(tBuC_5H_4)_2Yb(THF)_2][BPh_4]$ [141], $(tBuC_5H_4)_2Yb(\mu\text{-}H_2)AlH(Et_2O)$ by Bulychev [142] and with binary systems such as $Gd(RCOO)_3/Al(iBu)_3$ [143] and $Cp^*{}_2NdCl_2Li(OEt_2)_2/Mg(n,s\text{-}Bu)_2$ [144], to give in each case atactic polymers.

2.4.2. *Highly active, non-stereospecific group 3 styrene polymerization catalysts*

On the other hand, the lanthanide half-sandwich complex $Cp^*La(CH(SiMe_3)_2)_2(THF)$ (**99**, Fig. 9) was shown to promote styrene polymerization in the absence of any co-catalyst under relatively mild conditions (50 °C, toluene, 24 h, 80% yield for [St]/[La] = 100) to give rather low molecular weight polymers but with a narrow polydispersity (M_n = 7000–15,000 g/mol, M_w/M_n = 1.6) and a mostly atactic microstructure (*rr* = 51%) [145]. Similar oligomerization performances, with somewhat higher activities, were reported upon using simple binary $Ln[BH_4]_3/MgR_2$ systems [146].

Higher activities were observed with Nd and Yb-guanidinate complexes (**100–101**), as expected for complexes supported by bidentate ligand without bulky Cp^*. These complexes gave 60–100% yield within 10 min at 70–100 °C for [St]/[Ln] = 300–500 (activity ranging from 200 to 900 kg PS/(mol_{Ln} h)) and polystyrenes with higher molecular weights (M_n = 17,200–58,900 g/mol, M_w/M_n = 1.4–2.0) but still an atactic microstructure (*rr* < 53%) [147].

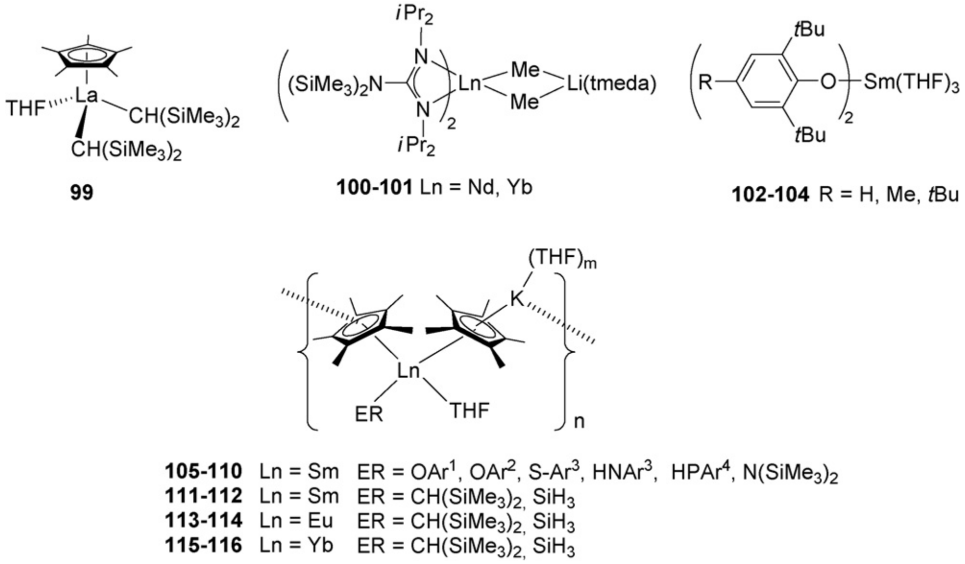


Fig. 9. Most active lanthanide-based catalysts used for non-stereoselective styrene polymerization [145–150].

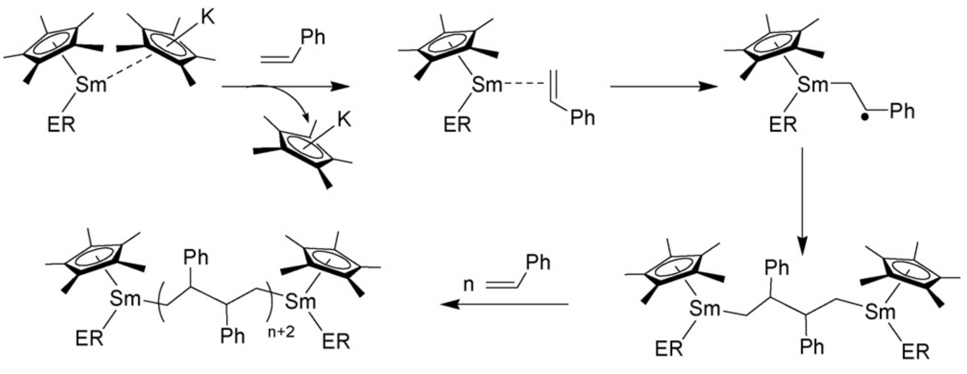
Interestingly, when polymerization of styrene by $Sm(OAr)_2(THF)_3$ (**102–104**) was carried out under high pressure ($P > 500$ MPa), a slight increase in the r dyads proportion ($P_r = 0.6$) was observed [148].

One of the highest activity at room temperature for styrene polymerization was reported with polymeric divalent Sm derivatives (**105–110**) $[Cp^*_2Sm(THF)_m(ER)(\mu\text{-}Cp^*)K(THF)_n]_x$ (ER = O-2,6-tBu-4-MeC_6H_2, O-2,6-$i$$PrC_6H_3$, S-2,4,6-$i$$PrC_6H_2$, HN-2,4,6-$i$$PrC_6H_2$, HP-2,4,6-$t$$BuC_6H_2$, $N(SiMe_3)_2$) (100% yield in 10–120 min for [St]/[Sm] = 700), yielding atactic materials with high molecular weight (M_n = 82,000–350,000 g/mol, M_w/M_n = 1.4–2.5) [149]. The activity was dependent on the ER ligand: the less sterically demanding O-2,6-$i$$PrC_6H_3$ and the more electron-donating amide gave the best results. More recently, alkyl and silyl analogues (**111–116**) were also reported to show high activity for styrene polymerization (100% conversion of 700 styrene eq. at room temperature within 5 min) and like with their parent complexes **105–110**, high molecular weight polymers were obtained (M_n = 42,000–140,000 g/mol, M_w/M_n = 1.2–3.2) [150]. As for other divalent lanthanide species, a one-electron transfer mechanism (Scheme 6) was proposed for those systems.

2.4.3. *Towards selectivity: Group 3 systems giving syndiotactic-enriched polystyrene*

Binary or ternary Nd-based systems incorporating carboxylate $Nd(C_5H_9(CH_2)_nCOO)_3/Al(i\text{Bu})_3$ (**117**, Fig. 10) or phosphate $Nd(O(O)P(OCH_2CH(Et)\ (CH_2)_3CH_3))_3/MgBu_2$/HMPA (**118**) were reported to give syndio-rich polystyrene with moderate activity [151,152]. Similar results were obtained with some MAO-activated lanthanidocenes (**119–123**) $(MeCp)_2Sm$(O-2,6-tBu-4-MeC_6H_2), Flu_2NdCl, Ind_2NdCl and $Me_2Si(Ind)_2NdCl$ [153]. Higher activities (100% yield in 0.3–3 h, in bulk or toluene at 20–75 °C, [St]/[Ln] = 3000–10,000) and higher molecular weights (M_n = 100,000–620,000 g/mol) were obtained with anionic tetrakis(allyl) complexes (**124–125**), still with predominant syndiotacticity (but not precisely determined) [154].

The "constrained-geometry" yttrium alkyl ($C_5Me_4SiMe_2$ NtBu)Y(μ-C_6H_{13})(THF) (**126**) also initiates styrene polymerization with moderate activity (100% yield in 24 h for [St]/[Y] = 130 at 25 °C) after partial THF removal. The obtained PS shows moderate molecular weight (M_n = 24,000–61,000 g/mol) with narrow polydispersity (M_w/M_n = 1.1–1.4) and a syndiotactic-enriched ($rr \approx 70\%$) but still amorphous microstructure (no T_m detected, T_g = 100 °C) [155].



Scheme 6. Proposed styrene polymerization mechanism with divalent Sm species [149].

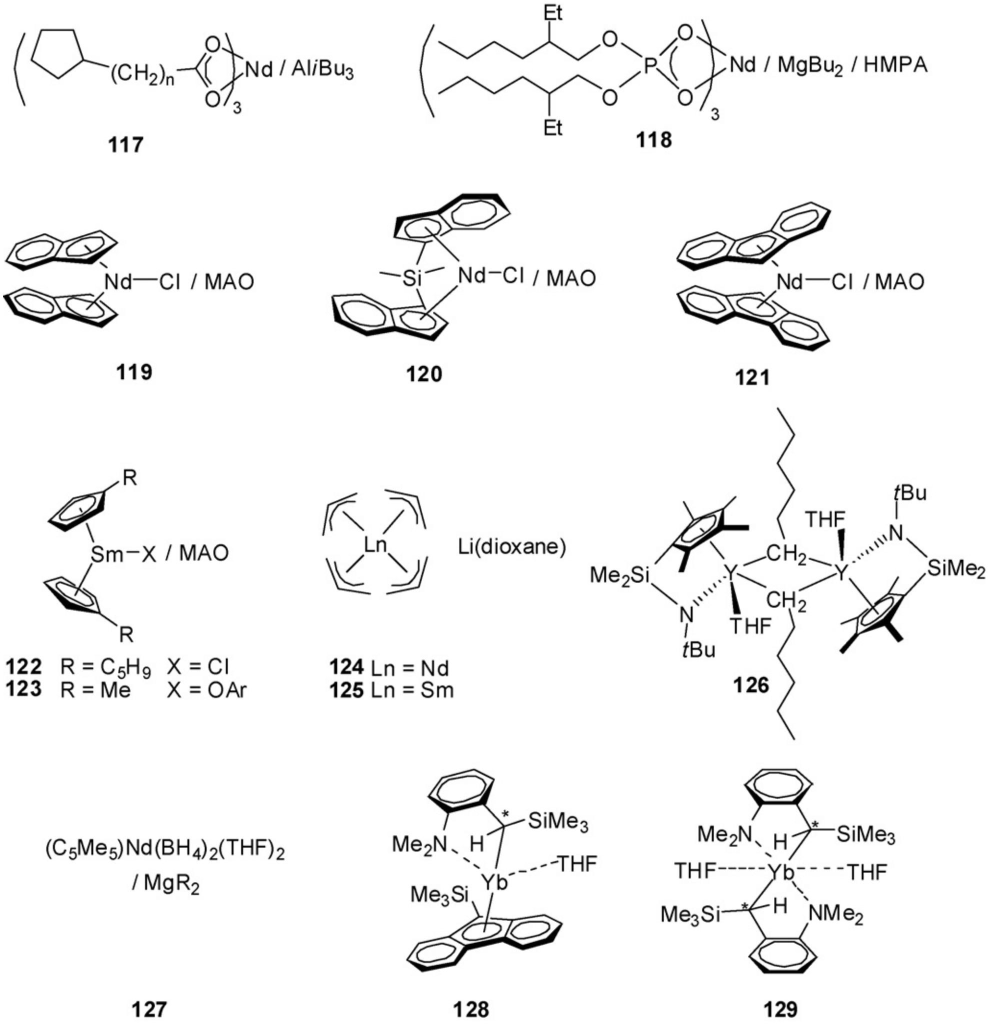


Fig. 10. Lanthanide-based catalysts and catalyst precursors used for the synthesis of syndiotactic-enriched polystyrene [151–157].

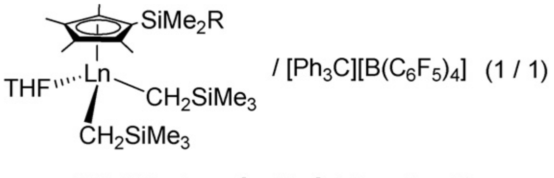
Also, binary combinations **127** of a bis(borohydride) Nd complex with an excess of a dialkylmagnesium reagent, which proceeds *via* reversible chain transfer between the two metal centers, afforded oligostyrenes with controlled molecular weights ($M_n = 560–16{,}000$ g/mol) and narrow distributions ($M_w/M_n = 1.2–1.3$) [156]. Contrary to the parent lanthanidocene system which provides atactic polystyrene [144, *vide supra*], syndiotactic enrichment of ca. 85% *r* was here observed.

A significant step forward was achieved by Harder with divalent ytterbium complexes [157]. The benzylamino-fluorenyl complex **128** polymerizes bulk styrene at 20 °C to afford moderately syndiotactic-enriched polystyrene (*r* = 82%, *rr* = 67%) and the bis(benzylamino) complex **129** leads to higher syndioselectivity (*r* = 93.1%, *rr* = 86.6% at 20 °C; *r* = 94.9%, *rr* = 90.0% at −20 °C). The polystyrenes had M_n in the range 51,000–200,000 g/mol with polydispersity consistent with a single-site behavior ($M_w/M_n = 1.8–2.3$). It was suggested that, in both cases, there are two growing chains per metal center. It is noteworthy that the Ca analogue of complex **128**, also quite active for styrene polymerization, affords syndiotacticity as high as that of **129**, while the Ca analogue of **129** leads to poorly syndiotactic-enriched polystyrene.

2.4.4. Syndiospecific group 3 catalysts

Highly syndiospecific styrene polymerization by lanthanide-based catalysts has only been achieved so far with two different catalytic systems that were published at about the same time in 2004. With those systems, the crude polymers contain neither atactic nor isotactic polystyrene. Therefore, solvent fractionation was not required to obtain pure sPS (*rrrr* > 99% for all polymers obtained).

First, the binary systems **130–133** based on lanthanide half-sandwich complexes (Fig. 11) were described by Hou and co-workers [158]. The neutral complexes alone did not show catalytic activity at room temperature in toluene solution. How-



130-133 Ln = Sc, Y, Gd, Lu R = Me

Fig. 11. Lanthanide half-sandwich catalysts used for syndiospecific styrene polymerization [158].

Table 2
Styrene polymerization catalyzed by complexes **130–133**[a] [158]

Ln	St/Ln	Time (min)	Yield (%)[b]	Activity (kg PS/(mol$_{Ln}$ h)	$M_n \times 10^{-3}$ (g/mol)[c]	M_w/M_n[c]	T_m (°C)[d]	Efficiency (%)[e]
Sc	500	1	100	3,125	88.5	1.4	271	58
Sc	700	1	100	4,376	119.6	1.3	271	61
Sc	1,000	1	100	6,034	135.5	1.4	272	77
Sc	1,500	1	100	9,362	189.6	1.5	271	82
Sc	2,000	1	100	12,498	269.4	1.4	272	77
Sc	2,500	1	87	13,618	378.6	1.4	273	60
Y	100	30	60	13	10.7	1.4	269	–
Gd	100	30	69	15	9.2	1.3	269	–
Lu	100	30	25	6	4.9	1.4	268	–

[a] Conditions: 21 μmol Ln, Ln/B = 1, toluene/styrene = 5:1 (volume), 25 °C.
[b] Weight of polymer obtained/weight of monomer used.
[c] Determined by GPC in 1,2-dichlorobenzene at 145 °C against PS standards.
[d] Determined by DSC.
[e] Catalyst efficiency = M_n calculated/M_n measured.

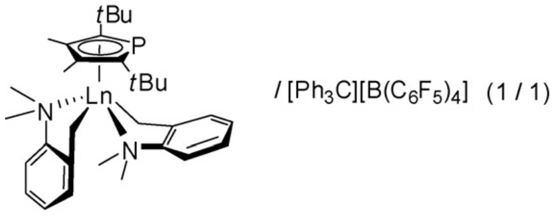
ever, when treated with one equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$], they all become highly active to give pure sPS (*rrrr* > 99%, no atactic or isotactic fraction was observed). The order of activity was found to be Sc ≫ Gd ≥ Y ≥ Lu (Table 2), with a striking contrast between Sc (up to 13.6 × 10^3 kg PS/(mol$_{Ln}$ h)) and the latter complexes (ca. 10 kg PS/(mol$_{Ln}$ h), i.e. a difference of three orders of magnitude). The observed activity is comparable with the most active Ti catalysts reported for syndiospecific styrene polymerization. The resulting polymer molecular weights increase almost linearly with the monomer/catalyst ratio while the polydispersity remains narrow. This denotes a very well-controlled polymerization with a "living" character [158].

The active species formed upon reaction of **130** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] is thought to be a cationic half-sandwich complex, as supported by ^{1}H NMR monitoring of the reaction: quantitative formation of Ph$_3$CCH$_2$SiMe$_3$ was instantly observed along with appearance of new resonances assigned to [(C$_5$Me$_4$SiMe$_3$)Sc(CH$_2$SiMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] [158]. Very recently, benzyl Sc congeners (C$_5$Me$_4$SiMe$_3$)Sc(CH$_2$Ph)$_2$(THF) were described but those complexes showed lower polymerization activity than complexes **130–133** [159].

In the same line, Nief and Hou reported very recently that cationic yttrium and scandium complexes, obtained upon activation of neutral mono(phospholyl)lanthanoid^{III} bis(dimethylaminobenzyl) complexes **134–135** with [Ph$_3$C][B(C$_6$F$_5$)$_4$], are very active for syndiospecific polymerization of styrene (Fig. 12) [160]. **134** gave excellent results (activity >3125 kg of sPS/(mol$_{Ln}$ h) at 25 °C; M_n = 300 000 g/mol; M_w/M_n = 2.07), that could be well compared with those reported for the C$_5$Me$_4$SiMe$_3$-ligated Sc bis(alkyl) complex **130**. The phospholyl ligand did not negatively influence the polymerization as it was observed for some group 4 catalysts. The activity observed for **135** was much higher than that for [(C$_5$Me$_4$SiMe$_3$)Y(CH$_2$SiMe$_3$)$_2$(THF)]/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (**131**). However, the activated analogous Sm complex did not show any activity under the same conditions, in accordance with a previous observation on the reactivity of monocyclopentadienyl complexes of the larger lanthanoids in styrene polymerization.

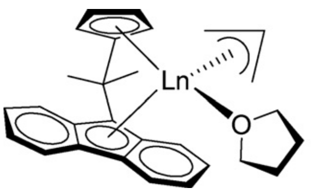
Note that cationic yttrium polyhydrido complexes derived from [Y$_4$(C$_5$Me$_4$SiMe$_3$)$_4$H$_8$(THF)$_n$] and [Ph$_3$C][B(C$_6$F$_5$)$_4$] were also briefly reported to produce highly syndiotactic polystyrene (ca. 10 kg of polystyrene per mol of Y and h, *rrrr* > 99%) [161].

Neutral allyl *ansa*-lanthanidocene complexes **136–139** (Fig. 13) developed by Carpentier and co-workers were also found to be active for highly syndiospecific styrene polymerization under mild conditions in the absence of any activator or co-catalyst, though with a maximal activity ca. one order of magnitude lower [162,163]. The apparent activity trend was Nd (**138**) ≫ Sm (**139**) > La (**137**) > Y (**136**). We assume it may reflect, at least in part, the instability of some of the complexes under the polymerization conditions, particularly in the case of lanthanum complex **137** that was found unstable in solution, even at room temperature; on the other hand, the neodymium system is very stable and allows polymerization up to 120 °C with excellent syndiotacticity and activity. The dependence of the molecular weights M_n *vs.* monomer conversion (Fig. 14) for



134-135 Ln = Sc, Y

Fig. 12. Phospholyl lanthanide half-sandwich catalysts used for syndiospecific styrene polymerization [160].



136 Ln = Y
137 Ln = La
138 Ln = Nd
139 Ln = Sm

Fig. 13. Allyl *ansa*-lanthanidocene single-component catalysts used for syndiospecific styrene polymerization [162,163].

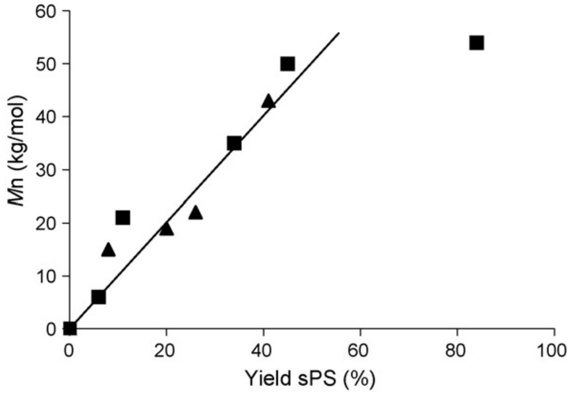


Fig. 14. Dependence of M_n *vs.* PS yield for styrene polymerization catalyzed by complexes **136** and **138** (▲: complex **136**, 60 °C, [St]/[Y] = 800, toluene solution; ■: complex **138**, 60 °C, [St]/[Nd] = 600, bulk) [163].

polymerization reactions initiated by the Y and Nd complexes **136** and **138**, in toluene solution and in bulk styrene, respectively, appears approximately linear in the first stage, indicative of a controlled polymerization, but show afterwards a saturation limit, likely reflecting transfer reactions (see Fig. 14 and Table 3).

The average number molecular weights of the sPS obtained with these systems are in the range 6000 to 135,000 g/mol. The molecular mass distributions are unimodal and rather narrow, usually ranging from 1.2 to 2.1, indicating a single-site catalyst behavior. Larger polydispersities ($2.1 < M_w/M_n < 5.2$), but still unimodal distributions, have been determined only for sPS samples produced over relatively long periods (usually > 60 min; entry 3) or at high monomer-to-catalyst ratios (entry 10), which may arise from either mass-transfer limitations and/or from gradual catalyst decomposition with time. The experimental M_n values are usually lower than those calculated (for $M_w/M_n < 1.3$), reflecting a moderate initiation efficiency for some of these catalysts.

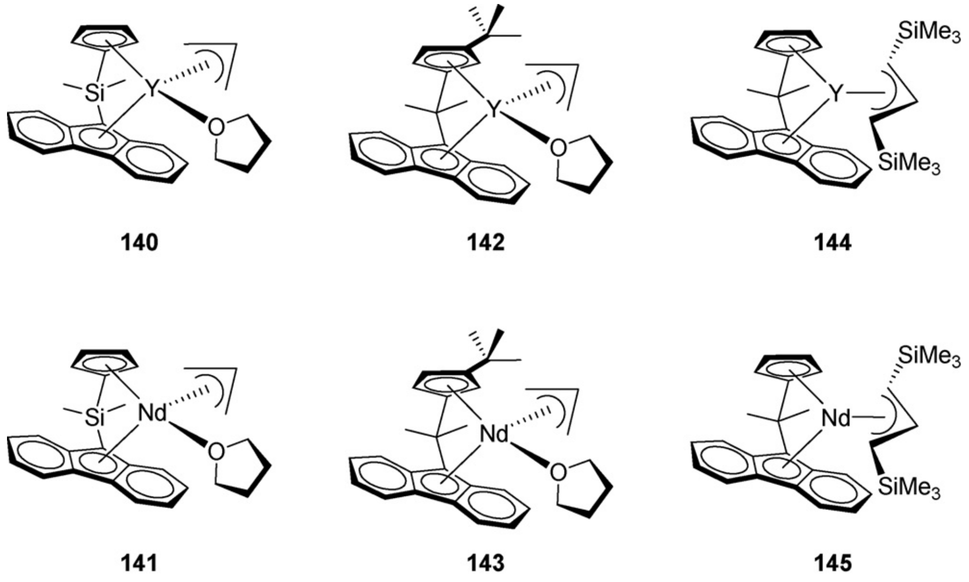
Rather low activities were observed when using Y and Nd complexes **140–141** (Fig. 15) featuring a silylene bridge (almost no activity detected with Y complex, activity up to 195 kg sPS/(mol$_{Ln}$ h) at 100 °C for Nd complex), as compared with their corresponding isopropylidene-bridged complexes **136** and **138** (up to 1710 kg sPS/(mol$_{Ln}$ h) at 60 °C). This drop of activity for both Y and Nd was tentatively related to the much larger bite angle of **140** and **141** (ca. 106°) as compared to their isopropylidene-bridged parent complexes (ca. 93–94°), rendering the coordination sphere of the metal center more hindered. Thus, the monomer approach and coordination are more difficult. The bite angle is also known to affect the global electronic features of complexes and consequently change their reactivity [164–166].

Complexes **142** and **143** bearing a 3-*tert*-butyl Cp ligand (Fig. 15) were found poorly active for styrene polymerization. Neither rising the polymerization temperature nor conducting the reaction for longer time periods did improve significantly the polymer yields. It is reasonable to assume that mostly steric features are at the origin of the decreased polymerization activity with these species. Most importantly, the introduction of the bulky 3-*tert*-butyl substituent on the Cp ligand did not modify the syndiospecificity of the system. This observation supports the chain-end control polymerization mechanism – unambiguously demonstrated by a statistic Bernoullian analysis – since **136** and **138** are C_s symmetric, while **142** and **143** display a C_1 symmetry, which, in analogy with propene polymerization, should lead to isotactic polymers *via* an enantiomorphic site control. However, one may point out that the singularly small bite angle (ca. 93–94°) in these allyl *ansa*-lanthanidocene com-

Table 3
Styrene polymerization catalyzed by complexes **136–145**[a] [1]

Complex	St/Ln	T_{polym} (°C)	Time (min)	Yield[b] (%)	Activity[c]	M_n[d] $\times 10^{-3}$ (g/mol)	M_w/M_n[d]	T_m[e] (°C)	Efficiency (%)[f]
136	800	20	120	26	10	24	2.3	260	90
136([g]	800	60	20	8	13	15	1.6	262	44
137	600	20	240	14	2	48	4.7	260	18
137	600	60	5	16	118	20	1.2	257	50
138	600	20	60	33	23	66	1.4	260	31
138	600	60	5	84	1,710	54	1.7	264	97
138	2,300	60	10	64	911	116	1.9	nd	132
139	600	60	5	28	218	27	1.5	262	65
140	500	60	2,880	13	<1	37	15.2	nd	18
141	500	60	35	35	32	24	1.9	255	76
141	800	100	5	21	195	9	1.9	251	194
142	2,000	60	1,440	1	<1	28	2.7	261	–
143	600	60	240	6	1	4	8.9	nd	94
143	500	60	60	2	1	nd	nd	nd	nd
144	500	60	60	4	2	nd	nd	255	nd
145	500	60	5	12	75	nd	nd	nd	nd

[a] General conditions: 30–70 μmol of Ln complex; 8.70 mol/L (bulk) styrene.
[b] Isolated yield of sPS collected after precipitation in MeOH.
[c] In kg sPS/(mol$_{Ln}$ h) calculated over the whole reaction time.
[d] Determined by GPC in 1,3,6-trichlorobenzene at 135 °C *vs.* PS standards.
[e] Melting temperature of PS measured by DSC.
[f] Catalyst efficiency = M_n calculated/M_n measured.
[g] Reactions carried out in toluene (5 mL). nd: not determined.



140 **142** **144**

141 **143** **145**

Fig. 15. Sylilene-bridged, Cp-substituted and allyl-substituted lanthanide complexes [163].

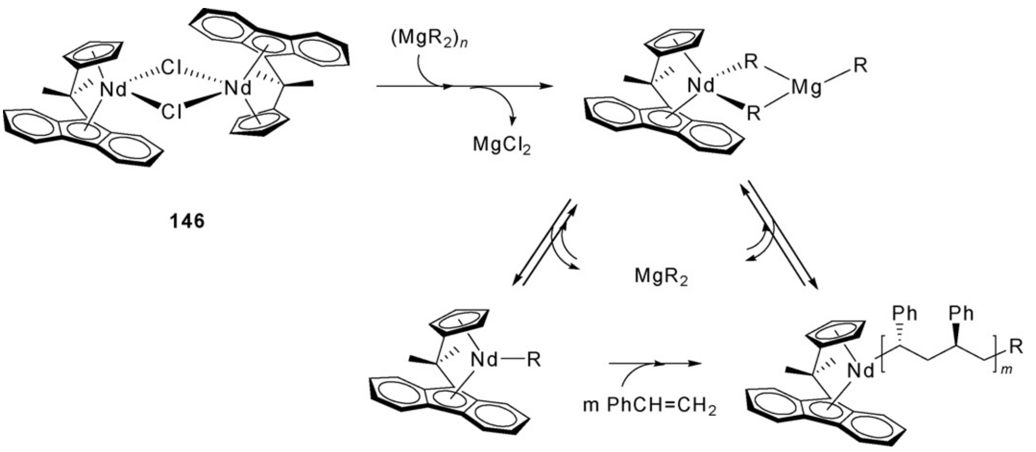
plexes might disturb this steric control by deviating upwards the orientation of the *tert*-butyl group and thus still allowing the monomer approach from this quadrant.

THF-free complexes **144** and **145** (Fig. 15) bearing a bulky (1,3-trimethylsilyl)allyl group did not exhibit better catalytic performances in spite of the absence of a donor molecule. Thus, it seems reasonable to assume that unlike the THF-adduct, the fluorenyl moiety is η^5-coordinated to compensate the electron deficiency and maintain the global electron count to 16 electrons [167]. On the other hand, the importance of steric factors cannot be ruled out: the bulky allyl group probably hinders the monomer approach and coordination, which results in a poor initiation efficiency of the catalyst. However, as discussed later in the case of isopropylidene-bridged bis(indenyl) systems for isospecific polymerization of styrene, such bulky allyl group does not preclude high polymerization activity.

Expectedly, the introduction of the bulky silyl substituents on the allyl group did not affect the stereoselectivity of the system. Indeed, the allyl group is assumed to be the initiation group and, as such, cannot influence the stereocontrol, independently of the polymerization mechanism (chain-end or site control mechanism) (*vide infra*).

In situ combinations of the *ansa*-chloroneodymocene precursor [(Cp-CMe$_2$-Flu)Nd(μ-Cl)]$_2$ (**146**) and a dialkylmagnesium (Mg(*n*-Bu)$_2$, Mg(allyl)$_2$; 1–100 eq. *vs*. Nd) were also investigated for styrene polymerization, to study chain transfer via transmetallation to excess dialkylmagnesium reagent (Scheme 7) [168]. Those binary systems are much less active than the parent single-component catalyst **138** (1–8 kg PS/(mol$_{\mathrm{Ln}}$ h) at 60 °C), but yield soluble oligostyrenes ($M_n = 1600$–$6500\ \mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.3$–2.5), which have a high degree of syndiotacticity ($r = 94\%$) and are selectively end-capped by butyl or allyl groups. The transmetallation efficiency remains however quite limited and significantly lower than that achieved from borohydride precursors [156].

The syndiospecific styrene polymerization mechanism with group 3 catalysts is generally admitted to be identical to that



Scheme 7. Synthesis of soluble syndiotactic oligostyrenes [168].

with group 4 metals. However, the styrene regioselectivity (primary *vs*. secondary insertion) with those metal centers is still being debated. Indeed, Bercaw and co-workers observed, for the reaction of styrene with the Sc hydrido complex $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}H)(PMe_3)]_2$, the formation of a primary styrene insertion followed by a secondary one to give $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH(Ph)CH_2CH_2\text{–}CH_2Ph)(PMe_3)]$ [169]. Similarly, Teuben reported the catalytic styrene dimerization with lanthanidocene hydrides to give the *trans*-1,4-diphenylbut-1-ene, i.e. the tail-to-tail coupling product [170]. Conversely, Okuda and co-workers observed exclusive secondary insertion of styrene with dimeric hydrido $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}H)(THF)]_2$ [155]. It was thus concluded that a second insertion of another styrene molecule is only possible with the less sterically hindered primary insertion product. This is consistent with DFT studies for titanocene catalysts which showed that primary insertion is favored in the initiation step but lead to a stable product that blocks additional primary insertions thus favoring secondary insertion in the propagation step [138]. However, the reason why those complexes are not reactive towards further secondary styrene insertions is not determined.

3. Isospecific styrene polymerization

Unlike sPS, isotactic polystyrene (iPS) has been previously efficiently synthesized by heterogeneous and anionic polymerization and is still best produced by these techniques that we will briefly review. Till quite recently, iPs remained a challenge for single-site polymerization catalysis.

3.1. Properties and applications of isotactic polystyrene

Pure isotactic polystyrene is a highly crystalline material presenting a melting temperature $T_m = 240\,°C$ [171]. However, its crystallization rate is very slow [172]. Thus, the reported values are often lower (ca 220 °C). iPS crystallizes into a 3/1 helical structure consisting of the regular repetition of *trans* and *gauche* conformation of the C–C backbone.

Compared to sPS, iPS has not found many industrial applications, mainly because of its slow crystallization rate.

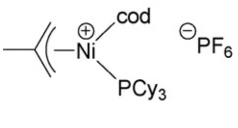
3.2. Isospecific homogeneous single-site catalysts

Although a small range of soluble catalysts have been reported to produce iso-enriched oligo- and polystyrenes, there are still very few true single-site catalysts that form pure iPS. These systems, which are mostly based on groups 3 and 4 metals, are presented below, with a brief extension to Ni.

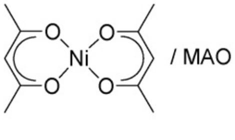
3.2.1. Systems giving isotactic-enriched polystyrene

Styrene oligomerization to isotactic-enriched ($m = 89\%$) oligomers ($M_n = 1900$ g/mol) was first reported with $[(\eta^3\text{-methallyl})Ni(\eta^4\text{-cod})]^+[PF_6]^-$ associated with tricyclohexylphosphine (PCy_3) (complex **147**, Fig. 16) [173,174]. The isolation of a cationic η^3-benzylic Ni complex (the insertion product of styrene into a Ni–H bond) along with minor ^{13}C resonances assigned to $\text{–}CH(C_6H_5)CH_3$ end-groups ruled out a cationic polymerization mechanism and indicated a secondary insertion mode of styrene. The influence of the phosphine ligands was then studied by varying their basicity and cone angles [175]. The activity was generally enhanced by the addition of a phosphorus ligand but decreased with increasing steric bulk and cone angles ($PMe_3 > PnBu_3 \gg PCy_3 > PtBu_3$). However, the best stereocontrol (up to $m = 90\%$) was provided by sterically demanding phosphines such as $P(o\text{-}Tol)_3$ or PCy_3. The obtained oligomers were found to bear an inverted tail-to-tail terminal group. This observation led the authors to propose a stereoregulation mechanism by combined effects of η^3-benzylic coordination of the growing chain and a high influence of a bulky ligand. Termination occurs by β-H elimination or chain transfer to monomer after a primary insertion of styrene [175].

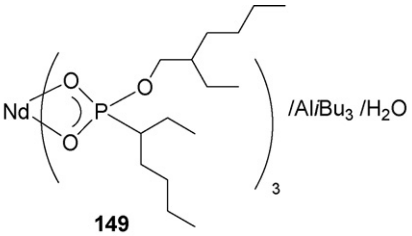
Contradictory results concerning the tacticity of the PS produced by the $Ni(acac)_2$/MAO system (**148**) have been published: it was first reported to yield atactic PS [35], but other authors stated that it gives moderately isotactic-enriched PS [176]. Detailed studies [177,178] revealed that free $AlMe_3$ present in MAO has a strong influence and induces a decrease both in



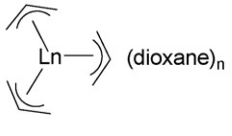
147



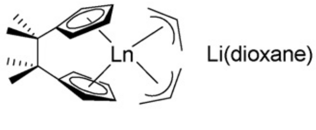
148



149



150 Ln = Nd n = 1
151 Ln = La n = 1.5



152 Ln = Sm
153 Ln = Nd

Fig. 16. Catalysts and catalysts precursors used for the synthesis of isotactic-enriched PS [154,175–178,181–183].

activity and stereospecificity: with increasing [Al]/[Ni] ratio, the polymer yield but also the isotactic *mmmm* pentads percentage decreases. This is thought to come from the formation of two types (iso- and aspecific) of active centers, the number of aspecific centers expanding more rapidly than the isospecific ones. Addition of NEt_3 reduces the activity but improves the polymerization stereospecificity, similar to the function of PCy_3 with (η^3-methallyl)Ni(η^4-cod). More, the heterogenization of the $Ni(acac)_2$ catalyst on MAO-coated silica allowed to further enhance the polymerization activity [179,180].

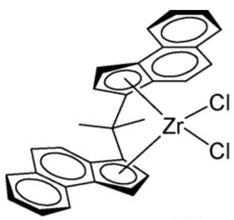
Apart from Ni complexes, lanthanides complexes were also reported to give isotactic-enriched polystyrene. The ternary system based on neodymium phosphonate complex $Nd(P_{507})_3$(**149**)/Al*i*Bu_3/H_2O ($P_{507} = CH_3(CH_2)_3CH(C_2H_5)CH_2–P(O)(O^-)–OCH_2CH(C_2H_5)–(CH_2)_3CH_3$) gives highly isotactic polystyrene, though along with about 50% of an atactic polymer fraction [181–183], an observation which calls for a multi-site behavior of this catalyst system. Polymerization performances are influenced by the [Al]/[Nd] and $[H_2O]/[Al]$ molar ratios, monomer and catalyst concentration and temperature. The optimum conditions were found to be [Al]/[Nd] = 6–8, $[H_2O]/[Al] = 0.05–0.08$, [styrene] = 5 mol/L, $[Nd] = 3.5–5 \times 10^{-2}$ mol/L, $T_{polym} = 70\,°C$ [182].

Moderate activities were obtained with neutral tris(allyl) neodymium complex **150** and anionic bis(allyl) *ansa*-lanthanidocenes **152–153** (60% conversion in 6–12 h at 50 °C) and pure isotactic PS was obtained after fractionation [154]. For the latter species, the authors suggested a disproportionation reaction to form *in situ* allyllithium and the neutral mono(allyl) *ansa*-complex, which was proposed to be the active species [154]. No explanation for the stereocontrol was given. However, these complexes, although achiral, feature a structure quite close to Brintzinger's catalyst and it seems reasonable to think that an enantiomorphic site control might be operative.

3.2.2. *Isospecific catalysts*

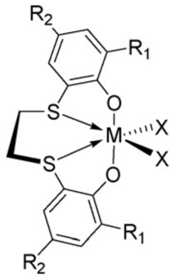
As already mentioned, isospecific styrene polymerization remained for a long time a challenge for homogeneous polymerization catalysis. As a matter of fact, there are, to date, only three systems reported to give pure iPS (*mmmm* > 0.9).

The first one, *rac*-isopropylidenebis(benzindenyl) zirconium complex (**154**, Fig. 17) activated by MAO, briefly described by Arai et al. [184], is closely related to Brintzinger's catalyst; i.e. the ligand framework presents a C_2 symmetry that is thought to induce stereocontrol by steric interactions with the growing polymer chain and the incoming monomer phenyl group. A high activity (333 kg iPS/(mol_{Zr} h)) was claimed under mild conditions (50 °C, toluene, 3 h, [Al]/[Zr] = 5500) and highly isotactic polystyrene was obtained according to ^{13}C NMR (*mmmm* > 0.9).



154

Fig. 17. Isopropylidenebis(benzindenyl) zirconium catalyst precursor used for isospecific styrene polymerization [184].



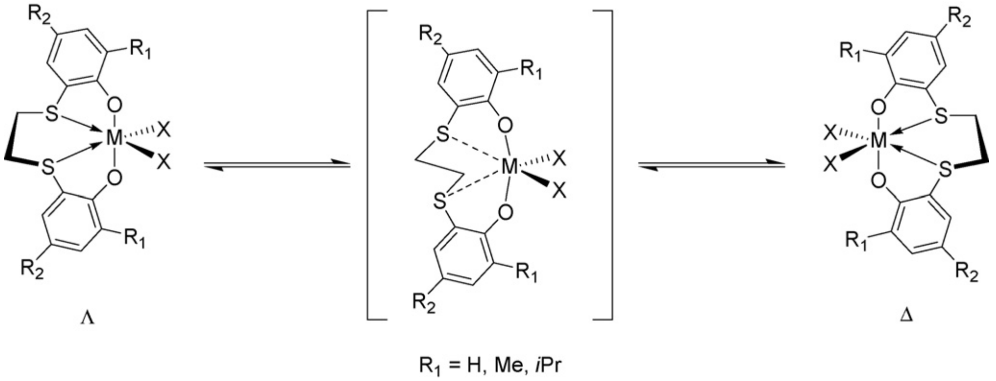
155-159	M = Ti	R_1 = H	R_2 = H, Me	X = Cl, O*i*Pr, Bz
160-161	M = Ti	R_1 = Me	R_2 = Me	X = Cl, O*i*Pr
162-163	M = Ti	R_1 = *i*Pr	R_2 = *t*Bu	X = Cl, O*i*Pr
164-172	M = Ti	R_1 = *t*Bu	R_2 = Me, OMe, *t*Bu	X = Cl, O*i*Pr, Bz
173-176	M = Ti	R_1 = cumyl	R_2 = Me, CMe_2Ph	X = Cl, O*i*Pr
177	M = Zr	R_1 = *t*Bu	R_2 = *t*Bu	X = Bz
178	M = Hf	R_1 = *t*Bu	R_2 = *t*Bu	X = Bz

Fig. 18. OSSO bis(phenolate) catalyst precursors used for isospecific styrene polymerization [66–69,185].

In 2003, Okuda and co-workers introduced a new class of post-metallocene catalysts based on a tetradentate dianionic OSSO bis(phenolate) ligand (Fig. 18) [66–69,185]. Due to the hemi-labile sulfide donor functions, those ligands induce stereochemical rigidity of the resulting complexes, as illustrated by the C_2 symmetry observed by NMR in solution and by X-ray diffraction in the solid state. However, the complexes bearing small *ortho* R_1 substituents (**155–163**) become fluxional at high temperature or even at room temperature for the di(isopropoxy) ones because of rapid interconversion between the Δ and Λ isomers, probably *via* a tetrahedral coordinated transition state (Scheme 8) [67–69]. Thus, the presence of bulky *ortho*-substituents (*t*Bu, cumyl) is essential for maintaining the configuration stability (up to 100 °C by NMR for R_1 = *t*Bu, cumyl), a feature which was found crucial for isospecific styrene polymerization. Indeed, upon activation with MAO, complexes bearing small *ortho*-substituents (**155–163**) gave, with low activity, atactic PS with broad molecular weight distribution, whereas complexes with large *ortho*-substituents gave pure isotactic PS with high activity (Table 4) [69].

The systems based on chloro precursors were generally found to be more active than the corresponding di(isopropoxy) ones and to give polymers with higher molecular weight (Table 4). The activity of the system based on complex **167** that has a *para*-methoxy group was significantly decreased compared to those based on **164** (*para*-methyl) and **170** (*para*-*t*Butyl), probably due to the electronic influence of the electron-releasing methoxy group [69]. The polydispersity indexes of the obtained iPS were narrow (ca. 2), as expected for single-site catalyst. The observed melting temperatures (ca. 220 °C) and ^{13}C NMR of the PS samples confirmed the pure isotactic microstructure.

When polymerization was performed in the presence of ^{13}C-enriched $AlMe_3$, the isolated polymer contained a labeled methyl end-group $CH(Ph)CH_2{}^{13}CH_3$. The chemical shift of $\delta = 11.8$ ppm in the ^{13}C NMR spectrum of this material indicates that the first insertion into the Ti–^{13}C bond occurred in a



Scheme 8. Interconversion between Λ and Δ isomers of OSSO bis(phenolate) complexes [67–69].

Table 4
Styrene polymerization catalyzed by complexes **164–178**[a] [66–69,185]

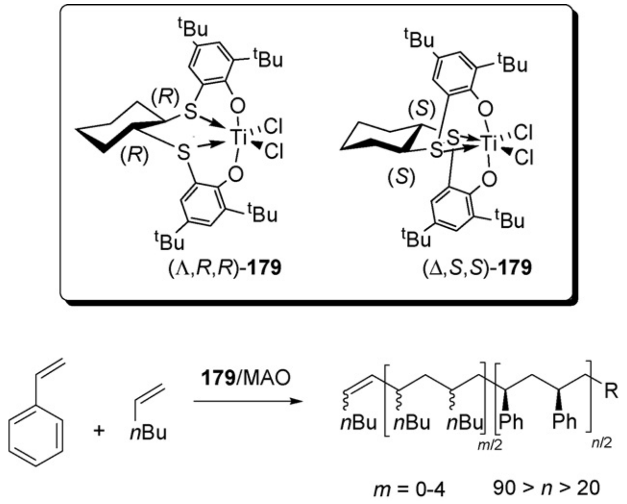
Complex (M)	R_1	R_2	X	Al/M	T_p (°C)	Time (h)	Activity (kg PS/(mol$_{Ti}$ h))	$M_n \times 10^{-3}$ (g/mol)[b]	M_w/M_n[b]	T_m (°C)[c]
164 (Ti)	*t*Bu	Me	Cl	1,500	40	2	1,813	1,013	1.6	222
165 (Ti)	*t*Bu	Me	O*i*Pr	1,500	40	2	18	573	1.9	217
166 (Ti)	*t*Bu	OMe	Cl	1,500	40	2	45	910	1.7	222
170 (Ti)	*t*Bu	*t*Bu	Cl	1,500	40	2	5,400	2,654	2.0	223
171 (Ti)	*t*Bu	*t*Bu	O*i*Pr	1,500	40	2	1,998	1,718	1.8	223
173 (Ti)	Cumyl	Me	Cl	500	50	1	613	700	1.9	225
174 (Ti)	Cumyl	Me	O*i*Pr	500	50	1	935	480	2.0	223
175 (Ti)	Cumyl	Cumyl	Cl	1,500	40	1	2,387	314	2.4	223
176 (Ti)	Cumyl	Cumyl	O*i*Pr	1,500	40	2	138	1,000	1.9	223
171 (Zr)	*t*Bu	*t*Bu	Bz	1,500	50	2	77	163	1.9	218
178 (Hf)	*t*Bu	*t*Bu	Bz	500	50	2	20	40	1.9	220

[a] Polymerization conditions: 2.5–100 μmol Ti complex, [St] = 1.75–3.5 mol/L (5–10 mL), toluene volume = 5–20 mL.
[b] Determined by GPC.
[c] Determined by DSC.

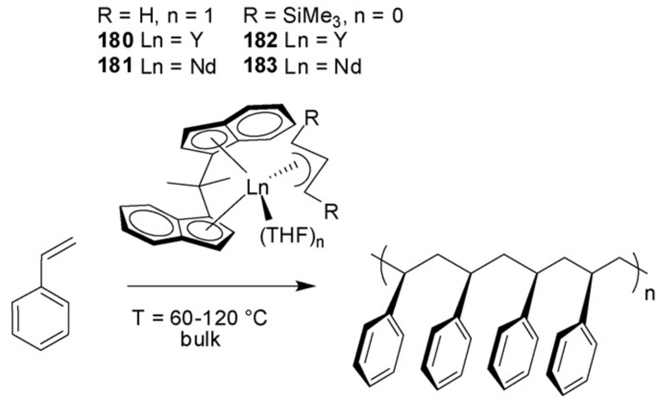
secondary fashion. In addition, the absence of any detectable head-to-head sequences suggests that the polymerization is highly regiospecific both in the initiation and the propagation step [66,68].

The active species for the MAO-activated complexes is assumed to be an alkyl cation $[(OSSO)TiR]^+$ in analogy to other polymerization mechanisms with non-metallocene catalysts. As a matter of fact, NMR monitoring of the reaction between the dibenzyl complex **171** and $B(C_6F_5)_3$ in bromobenzene indicated the formation of the thermally sensitive benzyl cation [185]. Furthermore, when activated by $[HNMe_2Ph][B(C_6F_5)_4]$ in the presence of Al(*n*Oct)$_3$, the dibenzyl complexes showed a living behavior: the polymer molecular weight increased linearly with conversion while polydispersity remained low ($M_w/M_n < 1.2$). Activation by $B(C_6F_5)_3$ was found possible but led to slightly broader molecular weight distributions, probably because of the stronger coordinating character of the counteranion [185].

The authors also recently achieved the synthesis of enantiomerically pure and optically active variants of the abovementioned catalyst precursors by introducing a *trans*-1,2-cyclohexanedyil backbone for the S–C–C–S bridge [186,187]. This chiral backbone led to the formation of a single configuration (helicity) at the titanium center, with one enantiomeric pair of the diastereomeric complex (Λ,*R*,*R*)-**179** and (Δ,*S*,*S*)-**179** (Scheme 9). They took advantage of their post-metallocene catalyst preference towards vinyl-aromatic monomers vis-à-vis α-olefins which, under copolymerization conditions, act as an "interrupter" of isotactic polystyrene chains. Thus, by adjusting the styrene/α-olefin (1-hexene) ratio, a series of isotactic oligostyrenes terminated by few hexene units was readily



Scheme 9. Chiral catalyst precursor **179** for the synthesis of optically active isotactic oligostyrene [186].



Scheme 10. Isospecific styrene polymerization catalyzed by bridged bis(indenyl) complexes **180–183** [188].

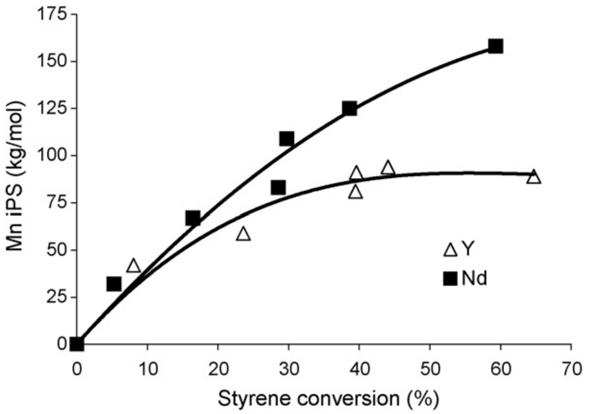


Fig. 19. Dependence of M_n *vs.* PS yield for styrene polymerization catalyzed by complexes **180** (△) and **181** (■) (60 °C, St/Ln = 500, bulk) [188].

prepared with the (Λ,*R*,*R*)-**179** and (Δ,*S*,*S*)-**179** complexes (Scheme 9), and the dependence of the specific rotation values on the molecular weight of the iPS further studied.

As anticipated, measurable optical activity in solution was detected only for low molecular weight materials, with a threshold corresponding to ca. 45 styrene units. A monotonous evolution of the optical activity was evidenced, which substantially complements the few discrete data thus far available. Also, the sign of optical rotation of oligomers depends on the configuration of the enantiomeric titanium catalyst used, confirming that prochiral monomer insertion into the titanium–alkyl bond is controlled by the chirality within the helical coordination sphere; i.e. an enantiomorphic site control is operative mechanistically speaking [186,187].

Recently, parent complexes of the neutral allyl *ansa*-lanthanidocenes abovementioned but incorporating an isopropylidene-bridged bis(indenyl) ligand coordinated in a *rac* fashion (**180–183**, Scheme 10) have been reported by Carpentier and co-workers to give highly isotactic polystyrene [188]. Representative results are given in Table 5.

The overall activity of these single-component catalysts [i.e., no activator is needed] is in the range 40–500 kg iPS/(mol$_{\text{Ln}}$ h) and expectedly increases with temperature. Noteworthy, the catalysts appear stable at least up to 120 °C, which is a particularly interesting feature in terms of industrial process. Expectedly, higher polymerization temperatures induce a decrease of the M_n values and a slight broadening of the polydispersities due to easier termination (β-H elimination) and transfer reactions.

Somewhat lower catalytic activities were achieved when polymerizations were carried out in cyclohexane solutions (entries 6, 7 and 10), but the recovered polymers showed very similar molecular weights and polydispersities.

Surprisingly, yttrium complex **180** was found to be slightly more active than its neodymium congener **181**. This activity trend contrasts with our previous observations on syndiospecific styrene polymerization with (CpCMe$_2$Flu)Ln(allyl)(THF) catalysts **136–140**, for which a dramatic difference between neodymium (most active) and yttrium (very poorly active) complexes was evidenced. It seems quite delicate to find a logical explanation for this phenomenon: although the most active catalysts in a wide array of polymerizations (ethylene, styrene, diene) often proved to be based on neodymium (and sometimes also samarium), there is no general rule. For instance, Hou and co-workers observed that scandium systems are significantly more active for syndiospecific styrene polymerization than other group 3 and lanthanide metal centers and no obvious relationship exists with ionic radii (*vide supra*) [158].

The controlled nature of these systems was again illustrated by the monotonous dependence of the molecular weights M_n *vs.* monomer conversion at 60–80 °C. As illustrated in Fig. 19., in the case of catalysts **180** and **181**, the M_n values increase almost linearly for the neodymium catalyst, at least in the first stage of the polymerization, but show for the yttrium catalyst a saturation limit, likely reflecting that transfer processes take place under those conditions. GPC traces of the polymers were all monomodal with moderately narrow molecular weight distributions, indicative of a single-site behavior. Catalysts **180** and **181** induced narrow polydispersities (typically, $M_w/M_n = 1.5$–2.0) but the experimental average number molecular weights M_n were systematically lower than the values calculated from the monomer-to-catalyst ratio and conversion, indicating a moderate initiation efficiency.

The THF-free complexes **182** and **183** featuring a bulky (1,3-trimethylsilyl)allyl group exhibit a slightly higher activity (up to 1600 kg iPS/(mol$_{\text{Ln}}$ h) at 120 °C) but led to somewhat broader polydispersities (typically, $M_w/M_n = 2.2$–2.6 *vs.* 1.5–2.0 with **180–181**), a feature that could be assigned to an easier initiation thanks to a less bulky allyl group in the latter case. This hypothesis was confirmed by ^{1}H NMR monitoring of the addition of 3 eq. of styrene to a solution of **176** in cyclohexane-d_{12} that showed that styrene insertion proceeds faster than initiation from 25 °C but that only a tiny part of the catalyst is active under those conditions.

Similar to the observations made with complexes **180–181**, the dependence of the polymer molecular weights M_n *vs.* conversion for complex **182** showed a saturation limit illustrated by a plateau at ca. $M_n = 85{,}000$ g/mol. Noteworthy, for polymerization catalyzed by this complex featuring a bulky allyl moiety, the experimental M_n values are higher than the ones calculated from the monomer-to-catalyst ratio and conversion, thus corroborating the poor initiation efficiency of this complex.

Table 5
Styrene polymerization catalyzed by bridged bis(indenyl) complexes **180–183**[a] [188]

Entry	Complex	[St]/[Ln]	T (°C)	Time (min)	Yield (%)	Activity (kg/(mol h))	M_n[b] × 10^{-3} (g/mol)	M_w/M_n[b]
1	**180**	600	60	30	57	66	65	1.5
2	**180**	500	80	15	87	181	58	1.8
3	**180**	1,200	80	20	37	135	74	1.8
4	**180**	500	100	5	92	527	26	1.7
5	**180**	400	120	5	88	463[c]	28	2.0
6	**180**([d]	500	60	60	42	23	56	1.7
7	**180**([d]	500	60	60	58	27	59	1.6
8	**181**	600	60	45	56	49	102	1.6
9	**181**	600	100	5	43	307	52	1.6
10	**181**([d]	600	60	60	26	16	87	1.5
11	**182**	450	60	8	11	39	59	2.2
12	**182**	460	80	4	95	685	46	2.4
13	**182**	4,600	80	21	78	1,066	35	2.6
14	**182**	420	100	2	98	1,279	22	2.5
15	**182**	480	120	2	100	1,637	12	3.4
16	**183**	500	60	8	100	392	71	2.6
17	**183**	520	80	6	100	600	56	2.5
18	**183**	480	100	5	100	1,094	36	2.3

[a] General conditions: 12–40 μmol Ln, total volume 1–20 mL, [St] = 8.70 mol/L (neat).

[b] M_n and M_w determined by GPC in THF *vs*. PS standards.

[c] Reaction time was not optimized.

[d] [St] = 4.35 mol/L styrene:hexane = 1:1 (volume).

All those complexes demonstrated outstanding stereospecificity, even for polymerization temperature up to 120 °C: the recovered polymers showed virtually no stereo-defects, a fact that hampered statistic analysis and mechanism determination and only allowed us to speculate on a pure enantiomorphic mechanism. Apart from the origin of the stereocontrol, the global data are consistent with a mechanism closely related to that proposed for the syndiospecific polymerization of styrene with the parent neutral *ansa*-lanthanidocenes (CpCMe$_2$Flu)Ln(allyl)(THF). In particular, the role of the allyl group appears essential for the initiation step.

Thus, these allyl *ansa*-lanthanidocene species turned out to be efficient single-component catalysts for highly stereospecific polymerization of styrene operable under industrially relevant conditions (bulk, 60–120 °C). The efficient control over the polymerization process peculiar to this unique catalytic system allows preparing highly stereoregular polymers with broad range of molecular weights and distributions. Furthermore, the polymer stereochemistry could be switched from syndiotactic to isotactic by a simple ligand geometry change, which constitutes to our knowledge the first example for styrene polymerization.

4. Concluding remarks

Although styrene is one of the few monomers able to polymerize through all the known polymerization mechanisms, there have been, until very recently, no general methods to control the stereoselectivity, even using coordinative-insertive polymerization.

Consequently to its late discovery, syndiotactic polystyrene has been the scope of many studies and similar to the work done with other α-olefins, the catalysts structure moved from metallocene to post-metallocene. Although most of the catalytic systems developed for the syndiospecific polymerization of styrene are titanium-based, the active species remains elusive but many mechanistic aspects could be well established. Lanthanides-based catalysts also proved to be highly active, mainly under somewhat more severe conditions (>50 °C, high pressure). However, some recent results show that they have a high potential as stereospecific catalysts.

On the other hand, isotactic polystyrene has been known for a longer time but did not arouse as many efforts as sPS. As a matter of fact, only a few catalytic systems are reported to give iPS. As for propene polymerization, it appears that C_2 catalyst symmetry is necessary to obtain an isotactic microstructure.

Thus, it seems that the correlation between catalyst structure and polymer stereochemistry established in the case of α-olefins is also valid for styrene, as illustrated by the results obtained with allyl *ansa*-lanthanidocene complexes.

References

[1] J.-M. Marechal, S. Carlotti, L. Shcheglova, A. Deffieux, Polymer 45 (2004) 4641 (Radical and ionic pathways do not allow a fine control of the polymerization stereochemistry, leading essentially to atactic polystyrene. Only under special conditions, isotactic-enriched polystyrene (mm up to 85%) was recovered).
[2] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, J. Am. Chem. Soc. 77 (1955) 1708.
[3] G. Natta, P. Corradini, Makromol. Chem. 16 (1955) 77.
[4] G. Natta, J. Polym. Sci. 16 (1955) 143.
[5] R.J. Kern, H.G. Hurst, W.R. Richard, J. Polym. Sci. 45 (1960) 195.
[6] P. Ammendola, T. Tancredi, A. Zambelli, Macromolecules 19 (1986) 307.
[7] R. Mani, C.M. Burns, Macromolecules 24 (1991) 5476.
[8] M.L. Dias, A. Giarrusso, L. Porri, Macromolecules 26 (1993) 6664.
[9] Q. Sun, Y. Fan, S. Liao, J. Liu, F. Wan, J. Xu, Polymer 42 (2001) 4087.
[10] M.R. Riberio, M.F. Portela, A. Deffieux, H. Cramail, M.F. Rocha, Macromol. Rapid Commun. 17 (1996) 461.
[11] G. Xu, S. Lin, Macromol. Rapid Commun. 15 (1994) 873.

[12] R.C. Hiorns, A. Khoukh, P. Ghigo, S. Prim, J. Francois. Polymer 43 (2002) 3365.
[13] A. Zambelli, P. Ammendola, Prog. Polym. Sci. 16 (1991) 203.
[14] R. Po, N. Cardi, Prog. Polym. Sci. 21 (1996) 47.
[15] N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, J. Mol. Catal. A: Chem. 128 (1998) 167.
[16] C. Pellecchia, A. Grassi, Top. Catal. 7 (1999) 125.
[17] J. Schellenberg, N. Tomotsu, Prog. Polym. Sci. 27 (2002) 1925.
[18] N. Tomotsu, M. Malanga, J. Schellenberg, in: J. Scheirs, D.B. Priddy (Eds.), Synthesis of Syndiotactic Polystyrene. In Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers, Wiley & Sons, 2003, p. 363.
[19] S. Cimmino, E.D. Pace, E. Martuscelli, C. Silvestre, Polymer 32 (1991) 1080.
[20] O. Greis, Y. Xu, T. Asano, J. Petermann. Polym. 30 (1989) 590.
[21] L.C. Lopez, R.C. Cieslinski, C.L. Putzig, R.D. Wesson, Polymer 36 (1995) 2331.
[22] G. Guerra, V.M. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, Macromolecules 23 (1990) 1539.
[23] A.J. Pasztor, B.G. Landes, P.J. Karjala, Thermochim. Acta 177 (1991) 187.
[24] J.E. Mark, Polymer Data Handbook, Oxford University Press, New-York, 1999.
[25] T. Kawamura, N. Toshima, K. Matsuzaki, Macromol. Rapid Commun. 15 (1994) 479.
[26] J. Xu, J. Ouyang, Z. Fan, D. Chen, L. Feng, Y. Yang, Polym. J. 30 (1998) 720.
[27] F. Feil, S. Harder, Macromolecules 36 (2003) 3446.
[28] J. Schellenberg, H.-J. Leder, Adv. Polym. Technol. 25 (2006) 141.
[29] N. Ishihara, M. Kuramoto, M. Uoi, Idemitsu Kosan Co Ltd, JP Pat. 62,187,708 (1985).
[30] N. Ishihara, M. Kuramoto, M. Uoi, Idemitsu Kosan Co Ltd, EP Pat. 210,615 (1986).
[31] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Macromolecules 19 (1986) 2464.
[32] A. Zambelli, C. Pellecchia, L. Oliva, P. Longo, A. Grassi, Makromol. Chem. 192 (1991) 223.
[33] J.C.W. Chien, Z. Salajka, J. Polym. Sci., Part A: Polym. Chem. 29 (1991) 1253.
[34] J.C.W. Chien, Z. Salajka, S. Dong, Macromolecules 25 (1992) 3199.
[35] N. Ishihara, M. Kuramoto, M. Uoi, Macromolecules 21 (1988) 3356.
[36] A. Zambelli, L. Oliva, C. Pellecchia, Macromolecules 22 (1989) 2129.
[37] J.C.W. Chien, Z. Salajka, J. Polym. Sci., Part A: Polym. Chem. 29 (1991) 1243.
[38] G. Ricci, C. Bosisio, L. Porri, Macromol. Rapid Commun. 17 (1996) 781.
[39] W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, Macromolecules 30 (1997) 7647.
[40] A. Kucht, H. Kucht, S. Barry, J.C.W. Chien, M.D. Rausch, Organometallics 12 (1993) 3075.
[41] M.H. Lee, S.K. Kim, Y. Do, Organometallics 24 (2005) 3618.
[42] S.K. Noh, W. Jung, H. Oh, Y.R. Lee, W.S. Lyoo, J. Organomet. Chem. 691 (2006) 5000.
[43] K. Nomura, T. Komatsu, Y. Imanishi, Macromolecules 33 (2000) 8122.
[44] K. Nomura, A. Fudo, Catal. Commun. 4 (2003) 269.
[45] D.J. Byun, A. Fudo, A. Tanaka, M. Fujiki, K. Nomura, Macromolecules 37 (2004) 5520.
[46] K. Nomura, A. Tanaka, S. Katao, J. Mol. Catal. A: Chem. 254 (2006) 197.
[47] K. Nomura, K. Fujita, M. Fujiki, Catal. Commun. 5 (2004) 413.
[48] J. Chen, Y.-S. Li, J.-Q. Wu, N.-H. Hu, J. Mol. Catal. A: Chem. 232 (2005) 1.
[49] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, Macromolecules 26 (1993) 5822.
[50] T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 519 (1996) 21.
[51] Y. Kim, B.H. Koo, Y. Do, J. Organomet. Chem. 527 (1997) 155.
[52] T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 583 (1999) 11.
[53] O. Stojkovic, W. Kaminsky, Macromol. Chem. Phys. 205 (2004) 357.
[54] P. Foster, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 2404.
[55] N. Schneider, M.-H. Prosenc, H.-H. Brintzinger, J. Organomet. Chem. 545–546 (1997) 291.
[56] G. Xu, D. Cheng, Macromolecules 33 (2000) 2825.
[57] G. Xu, E. Ruckenstein, J. Polym. Sci., Part A: Polym. Chem. 37 (1999) 2481.
[58] M. Wedler, F. Knosel, M. Noltemeyer, F.T. Edelmann, U. Behrens, J. Organomet. Chem. 388 (1990) 21.
[59] R. Duchateau, C.T. van Wee, A. Meetsma, J.H. Teuben, J. Am. Chem. Soc. 115 (1993) 4931.
[60] J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 14 (1995) 1827.
[61] J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 14 (1995) 2106.
[62] D. Liguori, F. Grisi, I. Sessa, A. Zambelli, Macromol. Chem. Phys. 204 (2003) 164.
[63] D. Liguori, R. Centore, A. Tuzi, F. Grisi, I. Sessa, A. Zambelli, Macromolecules 36 (2003) 5451.
[64] C. Averbuj, E. Tish, M.S. Eisen, J. Am. Chem. Soc. 120 (1998) 8640.
[65] J. Okuda, E. Masoud, Macromol. Chem. Phys. 199 (1998) 543.
[66] C. Capacchione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moller, T.P. Spaniol, J. Okuda, J. Am. Chem. Soc. 125 (2003) 4964.
[67] C. Capacchione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moller, R. Manivannan, T.P. Spaniol, J. Okuda, J. Mol. Catal. A: Chem. 213 (2004) 137.
[68] K. Beckerle, C. Capacchione, H. Ebeling, R. Manivannan, R. Mulhaupt, A. Proto, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 689 (2004) 4636.
[69] C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T.P. Spaniol, J. Okuda, Organometallics 24 (2005) 2971.
[70] Y. Kim, E. Hong, M.H. Lee, J. Kim, Y. Han, Y. Do, Organometallics 18 (1999) 36.
[71] Y. Kim, Y. Han, J.-W. Hwang, M.W. Kim, Y. Do, Organometallics 21 (2002) 1127.
[72] Y. Kim, Y. Do, J. Organomet. Chem. 655 (2002) 186.
[73] A. Grassi, A. Zambelli, F. Laschi, Organometallics 15 (1996) 480.
[74] T.E. Ready, R. Gurge, J.C.W. Chien, M.D. Rausch, Organometallics 17 (1998) 5236.
[75] A. Grassi, S. Saccheo, A. Zambelli, F. Laschi, Macromolecules 31 (1998) 5588.
[76] E.F. Williams, M.C. Murray, M.C. Baird, Macromolecules 33 (2000) 261.
[77] W. Kaminsky, Y.-W. Park, Macromol. Rapid Commun. 16 (1995) 343.
[78] M.K. Mahanthappa, R.M. Waymouth, J. Am. Chem. Soc. 123 (2001) 12093.
[79] A. Grassi, C. Pellecchia, L. Oliva, F. Laschi, Macromol. Chem. Phys. 196 (1995) 1093.
[80] G. Xu, Macromolecules 31 (1998) 586.
[81] C. Pellecchia, P. Longo, A. Grassi, P. Ammendola, A. Zambelli, Makromol. Chem., Rapid Commun. 8 (1987) 277.
[82] A. Zambelli, P. Longo, C. Pellecchia, A. Grassi, Macromolecules 20 (1987) 2035.
[83] A. Zambelli, A.L. Segre, M. Farina, G. Natta, Makromol. Chem. 110 (1967) 1.
[84] P. Longo, A. Grassi, A. Proto, P. Ammendola, Macromolecules 21 (1988) 24.
[85] P. Longo, A. Proto, A. Zambelli, Macromol. Chem. Phys. 196 (1995) 3015.
[86] A. Zambelli, C. Pellecchia, L. Oliva, Macromol. Symp. 48/49 (1991) 297.
[87] R. Quyoum, Q. Wang, M.-J. Tudoret, M.C. Baird, D.J. Gillis, J. Am. Chem. Soc. 116 (1994) 6435.
[88] C. Pellecchia, D. Pappalardo, L. Oliva, A. Zambelli, J. Am. Chem. Soc. 117 (1995) 6593.
[89] Q. Wang, R. Quyoum, D.J. Gillis, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, Organometallics 15 (1996) 693.
[90] M.C. Baird, Chem. Rev. 100 (2000) 1471.
[91] D.J. Duncalf, H.J. Wade, C. Waterson, P.J. Derrick, D.M. Haddleton, A. McCamley, Macromolecules 29 (1996) 6399.
[92] L. Cavallo, G. Guerra, Macromolecules 29 (1996) 2729.

[93] R.E. Campbell, T.H. Newman, M.T. Malanga, Macromol. Symp. 97 (1995) 151.
[94] R. Po', N. Cardi, L. Abis, Polymer 39 (1998) 959.
[95] N. Tomotsu, N. Ishihara, Stud. Surf. Sci. Catal. 121 (1999) 269.
[96] C. Pellecchia, P. Longo, A. Proto, A. Zambelli, Makromol. Chem., Rapid Commun. 13 (1992) 265.
[97] H. Kucht, A. Kucht, M.D. Rausch, J.C.W. Chien, Appl. Organomet. Chem. 8 (1994) 393.
[98] A. Grassi, C. Lamberti, A. Zambelli, I. Mingozzi, Macromolecules 30 (1997) 1884.
[99] L.A. Castonguay, A.K. Rappe, J. Am. Chem. Soc. 114 (1992) 5832.
[100] G. Sini, S.A. Macgregor, O. Eisenstein, J.H. Teuben, Organometallics 13 (1994) 1049.
[101] T. Yoshida, N. Koga, K. Morokuma, Organometallics 14 (1995) 746.
[102] J.C.W. Lohrenz, T.K. Woo, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 12793.
[103] P. Margl, L. Deng, T. Ziegler, J. Am. Chem. Soc. 120 (1998) 5517.
[104] P. Margl, L. Deng, T. Ziegler, Organometallics 17 (1998) 933.
[105] L. Deng, T. Ziegler, T.K. Woo, P. Margl, L. Fan, Organometallics 17 (1998) 3240.
[106] A. Shiga, J. Mol. Catal. A: Chem. 146 (1999) 325.
[107] G. Moscardi, F. Piemontesi, L. Resconi, Organometallics 18 (1999) 5264.
[108] R.D.J. Froese, D.G. Musaev, K. Morokuma, Organometallics 18 (1999) 373.
[109] M.S.W. Chan, K. Vanka, C.C. Pye, T. Ziegler, Organometallics 18 (1999) 4624.
[110] P. Margl, L. Deng, T. Ziegler, J. Am. Chem. Soc. 121 (1999) 154.
[111] A. Muñoz-Escalona, J. Ramos, V. Cruz, J. Martínez-Salazar, J. Polym. Sci., Part A: Polym. Chem. 38 (2000) 571.
[112] K. Vanka, T. Ziegler, Organometallics 20 (2001) 905.
[113] E. Zurek, T. Ziegler, Organometallics 21 (2002) 83.
[114] Z. Xu, K. Vanka, T. Firman, A. Michalak, E. Zurek, C. Zhu, T. Ziegler, Organometallics 21 (2002) 2444.
[115] L. Perrin, L. Maron, O. Eisenstein, D.J. Schwartz, C.J. Burns, R.A. Andersen, Organometallics 22 (2003) 5447.
[116] T. Wondimagegn, Z. Xu, K. Vanka, T. Ziegler, Organometallics 23 (2004) 3847.
[117] T. Wondimagegn, K. Vanka, Z. Xu, T. Ziegler, Organometallics 23 (2004) 2651.
[118] K. Vanka, Z. Xu, T. Ziegler, Organometallics 23 (2004) 2900.
[119] Z. Xu, K. Vanka, T. Ziegler, Organometallics 23 (2004) 104.
[120] K. Vanka, Z. Xu, T. Ziegler, Organometallics 24 (2005) 419.
[121] K. Vanka, Z. Xu, M. Seth, T. Ziegler, Top. Catal. 34 (2005) 143.
[122] S. Tomasi, A. Razavi, T. Ziegler, Organometallics 26 (2007) 2024.
[123] L. Deng, T.K. Woo, L. Cavallo, P.M. Margl, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 6177.
[124] L. Deng, P. Margl, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 1094.
[125] R.D.J. Froese, D.G. Musaev, K. Morokuma, J. Am. Chem. Soc. 120 (1998) 1581.
[126] A. Michalak, T. Ziegler, Organometallics 18 (1999) 3998.
[127] L. Deng, P. Margl, T. Ziegler, J. Am. Chem. Soc. 121 (1999) 6479.
[128] D. Musaev, K. Morokuma, Top. Catal. 7 (1999) 107.
[129] M.S.W. Chan, L. Deng, T. Ziegler, Organometallics 19 (2000) 2741.
[130] A. Michalak, T. Ziegler, Organometallics 19 (2000) 1850.
[131] T.K. Woo, P.E. Blochl, T. Ziegler, J. Phys. Chem. A 104 (2000) 121.
[132] A. Michalak, T. Ziegler, J. Am. Chem. Soc. 124 (2002) 7519.
[133] A. Michalak, T. Ziegler, Macromolecules 36 (2003) 928.
[134] G. Minieri, P. Corradini, A. Zambelli, G. Guerra, L. Cavallo, Macromolecules 34 (2001) 2459.
[135] G. Minieri, P. Corradini, G. Guerra, A. Zambelli, L. Cavallo, Macromolecules 34 (2001) 5379.
[136] I.E. Nifant'ev, L.Y. Ustynyuk, D.V. Besedin, Organometallics 22 (2003) 2619.
[137] S.H. Yang, J. Huh, J.S. Yang, W.H. Jo, Macromolecules 37 (2004) 5741.
[138] S.H. Yang, J. Huh, W.H. Jo, Organometallics 25 (2006) 1144.
[139] R.R. Thomas, V. Chebolu, A. Sen, J. Am. Chem. Soc. 108 (1986) 4096.
[140] Y.X. Cheng, Q. Shen, Chin. Chem. Lett. 4 (1993) 743.
[141] F. Yuan, Q. Shen, J. Sun, J. Organomet. Chem. 538 (1997) 241.
[142] S.Y. Knjazhanski, E.S. Kalyuzhnaya, L.E. Elizalde Herrera, B.M. Bulychev, A.V. Khvostov, A.I. Sizov, J. Organomet. Chem. 531 (1997) 19.
[143] E. Kobayashi, S. Kaita, S. Aoshima, J. Furukawa, J. Polym. Sci., Part A: Polym. Chem. 32 (1994) 1195.
[144] S. Bogaert, J.-F. Carpentier, T. Chenal, A. Mortreux, G. Ricart, Macromol. Chem. Phys. 201 (2000) 1813.
[145] K. Tanaka, M. Furo, E. Ihara, H. Yasuda, J. Polym. Sci., Part A: Polym. Chem. 39 (2001) 1382.
[146] P. Zinck, M. Visseaux, A. Mortreux, Z. Anorg, Allg. Chem. 632 (2006) 1943.
[147] Y. Luo, Y. Yao, Q. Shen, Macromolecules 35 (2002) 8670.
[148] Y. Zhang, Z. Hou, Y. Wakatsuki, Macromolecules 32 (1999) 939.
[149] Z. Hou, Y. Zhang, H. Tezuka, P. Xie, O. Tardif, T.-a. Koizumi, H. Yamazaki, Y. Wakatsuki, J. Am. Chem. Soc. 122 (2000) 10533.
[150] Z. Hou, Y. Zhang, M. Nishiura, Y. Wakatsuki, Organometallics 22 (2003) 129.
[151] M. Yang, C. Cha, Z. Shen, Polym. J. 22 (1990) 919.
[152] L. Jiang, Z. Shen, Y. Zhang, F. Zhang, J. Polym. Sci., Part A: Polym. Chem. 34 (1996) 3519.
[153] L. Cui, X. Ba, H. Teng, L. Ying, K. Li, Y. Jin, Polym. Bull. 40 (1998) 729.
[154] D. Baudry-Barbier, E. Camus, A. Dormond, M. Visseaux, Appl. Organomet. Chem. 13 (1999) 813.
[155] K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228.
[156] P. Zinck, A. Valente, A. Mortreux, M. Visseaux, Polymer 48 (2007) 4609.
[157] S. Harder, Angew. Chem. Int. Ed. 43 (2004) 2714.
[158] Y. Luo, J. Baldamus, Z. Hou, J. Am. Chem. Soc. 126 (2004) 13910.
[159] J. Hitzbleck, K. Beckerle, J. Okuda, J. Organomet. Chem. 692 (2007) 4702.
[160] F. Jaroschik, T. Shima, X. Li, K. Mori, L. Ricard, X.F. Le Goff, F. Nief, Z. Hou, Organometallics 26 (2007) 5654.
[161] X. Li, J. Baldamus, M. Nishiura, O. Tardif, Z. Hou, Angew. Chem. Int. Ed. 45 (2006) 8184.
[162] E. Kirillov, C.W. Lehmann, A. Razavi, J.-F. Carpentier, J. Am. Chem. Soc. 126 (2004) 12240.
[163] A.-S. Rodrigues, E. Kirillov, C.W. Lehmann, T. Roisnel, B. Vuillemin, A. Razavi, J.-F. Carpentier, Chem. Eur. J. 13 (2007) 5548.
[164] J.C. Green, Chem. Soc. Rev. 27 (1998) 263.
[165] P.J. Shapiro, Coord. Chem. Rev. 231 (2002) 67.
[166] B. Wang, Coord. Chem. Rev. 250 (2006) 242.
[167] E. Kirillov, J.-Y. Saillard, J.-F. Carpentier, Coord. Chem. Rev. 249 (2005) 1221.
[168] A.-S. Rodrigues, E. Kirillov, B. Vuillemin, A. Razavi, J.-F. Carpentier, J. Mol. Catal. A: Chem. 273 (2007) 87.
[169] P.J. Shapiro, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, W.D. Cotter, J. Am. Chem. Soc. 116 (1994) 4623.
[170] W.P. Kretschmer, S.I. Troyanov, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 17 (1998) 284.
[171] P.J. Lemstra, T. Kooistra, G. Challa, J. Polym. Sci., Part A-2: Polym. Phys. 10 (1972) 823.
[172] J.N. Hay, J. Polym. Sci., Part A: Gen. Papers 3 (1965) 433.
[173] J. Ascenso, A.R. Dias, P.T. Gomes, C.C. Romão, D. Neibecker, I. Tkatchenko, A. Revillon, Makromol. Chem. 190 (1989) 2773.
[174] J.R. Ascenso, A.R. Dias, P.T. Gomes, C.C. Romao, Q.T. Pham, D. Neibecker, I. Tkatchenko, Macromolecules 22 (1989) 998.
[175] J.R. Ascenso, A.R. Dias, P.T. Gomes, C.C. Romao, I. Tkatchenko, A. Revillon, Q.-T. Pham, Macromolecules 29 (1996) 4172.
[176] P. Longo, A. Grassi, L. Oliva, P. Ammendola, Makromol. Chem. 191 (1990) 237.
[177] G.L. Crossetti, C. Bormioli, A. Ripa, A. Giarrusso, L. Porri, Macromol. Rapid Commun. 18 (1997) 801.
[178] R. Po, N. Cardi, R. Santi, A.M. Romano, C. Zannoni, S. Spera, J. Polym. Sci., Part A: Polym. Chem. 36 (1998) 2119.
[179] M.L. Dias, G.L. Crossetti, C. Bormioli, A. Giarusso, L.C. de Santa Maria, F.M.B. Coutinho, L. Porri, Polym. Bull. 40 (1998) 689.

[180] L.C. Ferreira, M.A.S. Costa, P.I.C. Guimaraes, L.C. de Santa Maria, Polymer 43 (2002) 3857.

[181] L. Liu, Z. Gong, Y. Zheng, X. Jing, Macromol. Rapid Commun. 18 (1997) 859.

[182] L. Liu, Z. Gong, Y. Zheng, X. Jing, J. Polym. Sci., Part A: Polym. Chem. 36 (1998) 1773.

[183] L. Liu, Z. Gong, Y. Zheng, X. Jing, H. Zhao, Macromol. Chem. Phys. 200 (1999) 763.

[184] T. Arai, T. Ohtsu, S. Suzuki, Polym. Prepr. 39 (1998) 220.

[185] K. Beckerle, R. Manivannan, T.P. Spaniol, J. Okuda, Organometallics 25 (2006) 3019.

[186] K. Beckerle, R. Manivannan, B. Lian, G.-J.M. Meppelder, G. Raabe, T.P. Spaniol, H. Ebeling, F. Pelascini, R. Mülhaupt, J. Okuda, Angew. Chem. Int. Ed. 46 (2007) 4790.

[187] J.-F. Carpentier, Angew. Chem. Int. Ed. 46 (2007) 6404.

[188] A.-S. Rodrigues, E. Kirillov, T. Roisnel, A. Razavi, B. Vuillemin, J.-F. Carpentier, Angew. Chem. Int. Ed. 46 (2007) 7240.