

Syndiospecific polymerization of styrene

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Abstract

The current development of the metallocene-based catalysts for syndiotactic polystyrene (SPS) has been reviewed. SPS is a new semi crystalline engineering thermoplastic with a crystalline melting point of 270°C. Because of its crystalline nature, SPS has high heat resistance, excellent chemical resistance and water/steam resistance. In this review, some mechanistic models for polymerization and stereoregulation, as well as the factors which affect the activity and stereospecificity of the catalysts, are discussed. © 1998 Elsevier Science B.V.

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1. Introduction

One of the most important achievements in the field of synthetic polymer chemistry during the past 50 years has been the discovery by Ziegler of coordination polymerization of polyethylene in 1953. Ziegler's discovery, together with the ensuing work on the polymerization of propylene and other α -olefins by Natta, has given rise to the development of new classes of catalysts and polymers. The commercial advantage is that polymer structure control could be achieved in the polymerization of such readily available and cheap monomers such as ethylene and propylene.

Controlling the molecular architecture of polymers, e.g., stereoregularity, is of practical importance both in the development of new polymers or tailor-made polymers and in the control of polymer properties. One of the most fascinating developments in the field of transition metal polymerization during recent years has been the discovery by Sinn and Kaminsky [1] of homogeneous metallocene based coordination polymerization catalysts. In contrast with the traditional Ziegler–Natta catalysts, the metallocene ligands allow monomer insertions in a very homogeneous manner. Due to this structural control, metallocene catalysts can be easily modified to control polymer stereoregularity, molecular weight and molecular weight distribution.

Since the discovery of the Ziegler–Natta catalyst systems in the early 1950's, extensive studies concerning the stereospecific polymerization of olefins have been carried out [2,3]. In most cases,

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Table 1

Structure and thermal properties of atactic, isotactic and syndiotactic polystyrene

	Atactic PS	Isotactic PS	Syndiotactic PS
Crystallization rate	non	slow	fast
T_g (°C)	100	99	100
T_m (°C)	non	240	270

polymerization of vinyl monomers leads to isotactic polymers. Syndiotactic polymers were relatively rare until recently. Isotactic polystyrene (IPS) which was produced by Natta in 1955 is a semi-crystalline polymer with a high melting point, 240°C [4–6]. Several companies have tried to commercialize this polymer, but the crystallization rate of IPS is too slow to be practical in injection molding.

Ishihara et al. succeeded in the synthesis of syndiotactic polystyrene (SPS) in 1985 [7,64–77]. This is the first known case of syndiospecific polymerization for styrene. The melting point of SPS is 270°C and its crystallization rate is much faster than that of IPS (Table 1, Fig. 1). Furthermore, the low specific gravity, low dielectric constant, high modulus of elasticity and excellent resistance to water and other chemical agents make SPS a promising material for a large number of applications in many market areas. Syndiotactic polystyrene is currently being commercialized by Idemitsu Petrochemical Co. Ltd. under the trade name XAREC and by Dow Chemical Co. under the trademark Questra.

In this paper, we will attempt to review recent developments of catalyst for syndiospecific polymerization of styrene.

2. Catalytic systems for SPS

2.1. Transition metal compounds

The syndiotacticity of SPS results from the homogeneous coordinative polymerization mechanism. Typically, Group IV transition metal complexes are utilized with co-catalysts such as methylaluminoxane (MAO) or pentafluorophenyl borate derivatives. Initial evaluations of various titanium com-

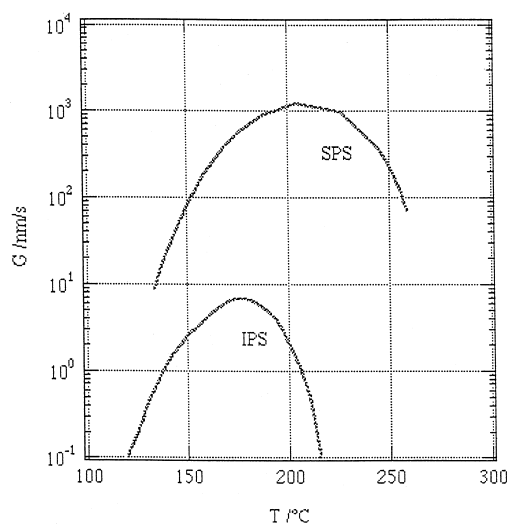


Fig. 1. Crystallization rate of syndiotactic polystyrene and isotactic polystyrene.

pounds with MAO have been published [7,8,64–77]. The results are shown in Table 2. Titanium halide compounds (e.g., TiCl_4 , TiBr_4 , CpTiCl_3 , Cp^*TiCl_3), and even titanium compounds lacking halogen atoms (e.g., $\text{Ti}(\text{OC}_2\text{H}_5)_4$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{Ti}(\text{N}(\text{C}_2\text{H}_5)_2)_4$, $\text{Ti}(\eta\text{-C}_6\text{H}_6)_2$ and $\text{CpTi}(\eta\text{-CH}_3\text{C}_6\text{H}_5)_2$) can produce SPS. Not only Ti(IV) but also Ti(III) compounds, such as $\text{CpTi}^{\text{III}}\text{Cl}_2$, give SPS. Zambelli et al. [8] reported that Ti(II) (e.g., $\text{Ti}(\text{Ph})_2$) also could produce SPS, but $\text{Ti}(\text{bipy})_3$, formally Ti(0), gave atactic PS. However, as shown in Table 2, Ti(0) arene compounds can produce SPS [10].

The catalytic activity was found to vary according to the ligands on the titanium. Among the SPS producing catalysts, titanocene complexes with one cyclopentadienyl ligand yield the highest activity for SPS. The polymerization activities for several substituted $\text{CpTi}(\text{OMe})_3$ complexes have been reported [11] as follows, in order of decreasing catalytic activity: $\text{EtMe}_4\text{CpTi}(\text{OMe})_3 > \text{Cp}^*\text{Ti}(\text{OMe})_3 > \text{Me}_3\text{SiMe}_4\text{CpTi}(\text{OMe})_3 > \text{Me}_4\text{CpTi}(\text{OMe})_3 > (\text{Me}_3\text{Si})_2\text{CpTi}(\text{OMe})_3 > \text{CpTi}(\text{OMe})_3$ (Table 3). The data indicate that substituents on the cyclopentadienyl ligand which are electron releasing generally yield higher polymerization activities. This result suggests stabilization of the active site by electron releasing substituents.

The polymerization activities in the presence of Cp^*TiR_3 compounds in which R is alkoxide and chloride ligands is as follows [11], in order of decreasing catalytic activity: $\text{Cp}^*\text{Ti}(\text{O}^i\text{Pr})_3$ and $\text{Cp}^*\text{Ti}(\text{OMe})_3 > \text{Cp}^*\text{Ti}(\text{OPh})_3 > \text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{CH}_3)_3 > \text{Cp}^*\text{TiCl}_3 > \text{Cp}^*\text{Ti}(\text{O}^t\text{Bu})_3 >$

Table 2
Polymerization of styrene using various metal compounds with MAO

Catalyst	[Al] mol	Conversion (wt%)	Stereospecificity
TiCl_4	0.04	4.1	syndiotactic
TiBr_4	0.04	2.1	syndiotactic
$\text{Ti}(\text{OCH}_3)_4$	0.04	3.8	syndiotactic
$\text{Ti}(\text{OC}_2\text{H}_5)_4$	0.04	9.5	syndiotactic
CpTiCl_3	0.015	68.2	syndiotactic
	0.03	99.2	syndiotactic
Cp_2TiCl_2	0.03	1.0	syndiotactic
$\text{C}_5(\text{CH}_3)_2\text{TiCl}_2$	0.03	2.0	syndiotactic
$\text{C}_5(\text{CH}_3)_2\text{TiClH}$	0.03	8.8	syndiotactic
$\text{Ti}(\eta\text{-C}_6\text{H}_6)_2$	0.025	5.4	syndiotactic
$\text{Ti}(\eta\text{-CH}_3\text{C}_6\text{H}_5)_2$	0.025	5.9	syndiotactic
$\text{Ti}(\eta\text{-(CH}_3)_2\text{C}_6\text{H}_6)_2$	0.025	5.7	syndiotactic
$\text{Ti}(\eta\text{-(CH}_3)_3\text{C}_6\text{H}_5)_2$	0.025	6.0	syndiotactic
$\text{Ti}(\text{acac})_2\text{Cl}_2$	0.04	0.4	syndiotactic
$\text{Ti}(\text{N}(\text{C}_2\text{H}_5)_2)_4$	0.04	0.4	syndiotactic
ZrCl_4	0.04	0.4 ^a	atactic
CpZrCl_3	0.04	1.3 ^a	syndiotactic
Cp_2ZrCl_2	0.04	1.3 ^a	atactic
Cp_2HfCl_2	0.04	0.7 ^a	atactic
Cp_2VCl_2	0.04	0.7 ^a	atactic
$\text{Nb}(\text{OC}_2\text{H}_5)_5$	0.04	0.2 ^a	atactic
$\text{Ta}(\text{OC}_2\text{H}_5)_5$	0.04	0.1 ^a	atactic
$\text{Cr}(\text{acac})_3$	0.01	1.8 ^b	atactic
$\text{Co}(\text{acac})_3$	0.01	1.8 ^b	atactic
$\text{Ni}(\text{acac})_2$	0.01	80.8 ^b	atactic
$\text{Ni}(\text{acac})_2$	0.04	31.0 ^c	isotactic

Polymerization conditions (see Refs. [7,8]); metal compounds 5×10^{-5} mol, styrene 23 ml, toluene 100 ml, at 50°C for 2 h.

^aMetal compounds 5×10^{-5} mol, styrene 23 ml, toluene 100 ml, at 50°C for 2 h.

^bMetal compounds 2.5×10^{-5} mol, styrene 50 ml, toluene 100 ml, at 50°C for 2 h.

^cSee Ref. [9]; metal compounds 3.3×10^{-5} mol, styrene 10 ml, toluene 10 ml, at room temperature for 20 h.

Table 3
Catalyst activities of substituted cyclopentadienyltitanium trimethoxide

Complex	Activity (kg-SPS/g-Ti)
CpTi(OMe) ₃	10
(Me ₃ Si) ₂ CpTi(OMe) ₃	25
Me ₄ CpTi(OMe) ₃	130
(Me ₃ Si)Me ₄ CpTi(OMe) ₃	135
Cp*Ti(OMe) ₃	200
EtMe ₄ CpTi(OMe) ₃	210

Cp*Ti(OⁱC₃HF₆)₃. The chloride ligand and the electron withdrawing alkoxide decrease the conversion as does the bulky *tert*-butoxide ligand. The methoxide, *iso*-propoxide, phenoxide and *p*-methylphenoxide are all similar in terms of conversion. Recently, Kaminsky showed that the catalytic activity of CpTiF₃ is better than CpTiCl₃ [12].

Ready et al. [13] observed that indenyltitanium trichloride, IndTiCl₃, is a significantly more active catalyst than CpTiCl₃. But Tomotsu et al. compared the two catalysts and found the catalytic activity of IndTiCl₃ to be lower than that of CpTiCl₃ [14]. Difference in polymerization conditions may account for the observed differences in catalyst performance. Furthermore, Chien et al. [15] investigated the influence of aromatic substituents on indenyl ligands. The results suggested that benzindene

Table 4
The effects of bite angle of Cp ligand on the catalyst performance

Catalysts	Stereoregularity	
	PP	PS
	Atactic	Syndiotactic [rrrr] = 1.0
	Atactic	Syndiotactic [rrrr] = 1.0
	Isotactic [mm] = 0.57	Syndiotactic [rrrr] = 1.0
	Atactic [mm] = 0.19	Atactic
	Isotactic [mm] = 0.52	Atactic
	Isotactic	Atactic
	Isotactic [m] = 0.96	Atactic

[Al]/[Ti] = 40, MAO (*n* = 16), [Ti] = 10 mM, at 15°C.

^aMM-2 calculated.

stabilized the active catalytic species more compared to the phenyl substitution on the C₅ ring for the indenyl ligand.

The polymerization activities for several ansa-titanocene complexes have been reported by Miyashita et al. [16] as follows, in order of decreasing catalytic activity: CH₂(Cp)₂TiCl₂ > SiMe₂(Cp)₂TiCl₂ > Me₂Si(Cp)₂TiCl₂ > C₂H₂(Cp*)₂TiCl₂ > (Cp*)₂TiCl₂ > Cp₂TiCl₂ (Table 4). The data indicate that the polymerization activity as well as syndiospecificity increase by decreasing the bite-angle, the angle of the Cp centroid–Ti–Cp centroid, in these ansa-titanocene compounds. The activity of ansa-titanocene complexes are less than that of monocyclopentadienyl complexes.

Ishihara et al. [10,17,18] investigated the relationship between the catalysts and the stereoregularities of the polypropylene and polystyrene obtained using several metallocenes activated with MAO (Table 5). Titanocenes produce atactic polypropylene and syndiotactic polystyrene and zirconocenes produce isotactic polypropylene and atactic polystyrene. The ansa-zirconocene compounds show lower activity and lower stereospecificity than the corresponding ansa-titanocenes. These results are consistent with the suggestion that the catalyst center and the mechanism of syndiospecific polymerization of styrene may be different from those of olefin polymerization in the formation of an active catalyst by the reaction with MAO.








It was first thought that only titanium compounds when combined with MAO gave pure SPS and much attention has been paid to developing more efficient catalysts. Later, Zr compounds (e.g., Zr(CH₂C₆H₅)₄ [19], Zr(η-C₇H₈)₂ [10], (acac)₂ZrCl₂, (Me₃CCOCHCO₂Me)₂ZrCl₂ [20]) were also found to catalyze syndiospecific styrene polymerization. In comparison with the Ti compounds, the Zr compounds show lower activity and lower stereospecificity, which could arise from the less electrophilic and larger ionic radius of zirconium in comparison with titanium.

Yang et al. [21] examined rare earth coordination catalysts. Nd(naph)₃/Al(*iso*-Bu)₃ catalyst system was found to produce syndiotactic-rich polystyrene. They proposed that the catalytically active species might be an ionic complex, because the addition of CCl₄ increased the catalytic activity.

Pyrazolylborate complexes of titanium [11] have been studied for SPS polymerization. Similarities between the cyclopentadienyl ligand and the hydridotris(pyrazolyl)borate ligand have been noted for transition metal complexes. Catalyst efficiencies are much lower than the analogous pentamethylcyclopentadienyl complex. This ligand may donate too much electron density to the titanium.

Table 5

Relationships between the catalysts and stereoregularities of the polypropylene and polystyrene products [15]

	Bite Angle (°)	Activity (g/g-Ti/Hr)	SPS/total PS (%)	Tacticity (<i>rrrr</i> %)
	131	21	11	94
	137	57	73	94
	121	573	96	99
	(121) ^a	1037	98	99
	(128) ^a	669	98	99
	(128) ^a	957	98	99
	131	38	11	95

The molecular weight of SPS can be controlled primarily by polymerization temperature, which sharply affects the rate of chain transfer via β -hydride elimination. As the polymerization temperature is increased, the SPS molecular weight decreases significantly. However, substituents on the cyclopentadienyl ring of the monometallocene titanium complexes can also affect the SPS molecular weight. A dramatic decrease in the molecular weight of the SPS produced with CpTiCl_3 is observed relative to that with Cp^*TiCl_3 . This would indicate that β -hydride elimination occurs more readily for CpTiCl_3 . The Cp^* ligand apparently stabilizes the active center and retards β -hydride elimination.

2.2. Co-catalysts

MAO is an important cocatalyst which activates the Group IV metallocenes in homogeneous Ziegler–Natta polymerization (Table 6). Before the discovery of MAO, the homogeneous Ziegler–Natta catalyst Cp_2TiCl_2 , activated with alkylaluminum, yielded atactic polystyrene with low catalytic activity. The use of MAO instead of alkylaluminum raised the catalyst activity by several orders of magnitude. MAO is routinely used for the synthesis of syndiotactic polystyrene [17]. A rapid alkylation of metallocene by MAO takes place, and the active species arises from a ligand transfer reaction between the metallocene alkyls and MAO. The active species formed from these reactions is probably in combination with a non-coordinating MAO anion.

Many researchers are trying to clarify the structure and roles of MAO. A higher degree of oligomerization of MAO provides a beneficial effect to the catalyst activity. Earlier research suggested that MAO might exist in a linear and a cyclic form. The role of MAO for syndiotactic polymerization of styrene was also examined by Miyashita [22]. MAO of different molecular weights were made by the distillation of normal MAO and the effects of molecular weight of MAO on the catalytic activity are examined. They found that $\text{Me}(\text{Al}(\text{Me})\text{O})_{15}\text{AlMe}_2$ showed the highest activity and a large amount of MAO was required. The structure of the reacted compound between titanocene and MAO was analyzed by ^{13}C - and ^1H -NMR and the structure in Fig. 2 was determined.

Table 6
Polymerization of styrene using CpTiCl_3 with various organoaluminum compounds [15]

Org. Al (mol dm ⁻³)	Yield (g)	Conv. (wt%)	Stereospecificity
—	0.8	0.5	Atact.
TMA (0.05)	0.1	0.1	Atact.
TEA (0.05)	0.2	0.1	Atact.
TISA (0.05)	0.1	0.1	Atact.
TMA (0.4) + H ₂ O (0.4)	17.6	10.8	Synd.
TEA (0.4) + H ₂ O (0.4)	0.8	0.5	Synd.
MAO (0.4)	14.9	9.2	Synd.
MAO (0.2) + TMA (0.2)	7.1	4.4	Synd.
MAO (0.2) + TEA (0.2)	0.3	0.2	Synd.
MAO (0.2) + TIBA (0.2)	15.5	9.5	Synd.
CIAO (0.4)	94.7	100	Atact.
$\text{Me}_2\text{AlOAlMe}_2^a$ (0.6)	0.1	0.1	Atact.
$(\text{Me}_2\text{AlO})_2\text{AlMe}^b$ (0.5)	0.1	0.1	Atact.
$(\text{Me}_2\text{AlO})_3\text{Al}^c$ (0.5)	0.3	0.2	Atact.
MAO ($M_w < 500$) (0.4)	Trace		Synd.
MAO ($M_w > 500$) (0.4)	14.9	9.2	Synd.

CpTiCl_3 5.0×10^{-4} mol dm⁻³, toluene 0.1 dm³, styrene 8.7 mol dm⁻³, 50°C, 2 h.

^a $\text{Me}_2\text{AlOLi} + \text{Me}_2\text{AlCl}$.

^b $2\text{Me}_2\text{AlOLi} + \text{MeAlCl}_2$.

^c $3\text{Me}_2\text{AlOLi} + \text{AlCl}_3$.

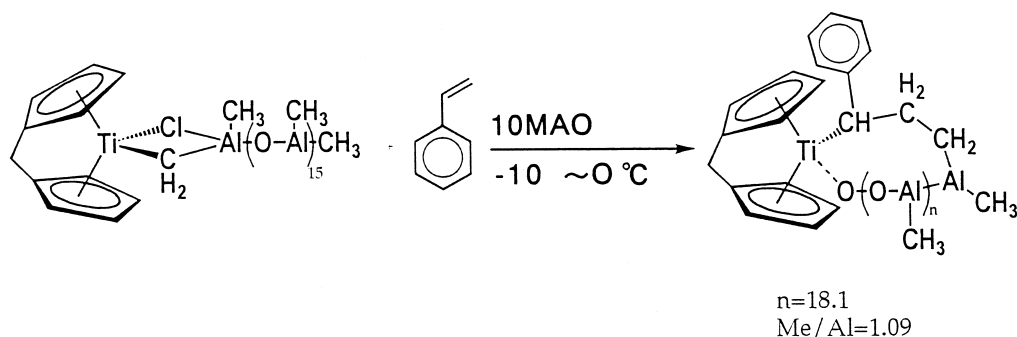


Fig. 2. Structure of zwitterionic Ti cation center.

Miyashita also examined the molar electric conductivity of the reacted compound between titanocene and MAO [23]. They found it was $0.006 \text{ S cm}^2/\text{mol}$ in toluene and concluded that the active site for polymerization must have the structure of zwitterionic Ti cation center.

MAO is known to contain trimethylaluminum (TMA) both in a form coordinated to MAO and as free TMA. Tomotsu et al. [24] examined the effects of TMA in MAO. They found it decreases the catalytic activity for SPS production (Fig. 3).

Perfluorophenyl borate derivatives have also been used as cocatalysts in SPS polymerizations. The reaction of $\text{CH}_2(\text{Cp})_2\text{Ti}(\text{Me})_2$ in equimolar mixture with dimethylaniliniumtetrakis(pentafluorophenyl)borate or tris(pentafluorophenyl)borane has been examined by Miyashita [25]. They isolated two types of methylene bis(cyclopentadienyl)titanium ion complexes (Fig. 4). These complexes were active in the polymerization of styrene but only atactic polystyrene was formed.

Baird et al. [26] examined the catalytic activity of Cp^*TiMe_3 with similar boranes. The polymer produced was a mixture of atactic and syndiotactic polystyrene. They examined the effect of polarity of solvent for polymerization by using CH_2Cl_2 and $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ and found that polar solvents increased the yield of atactic polystyrene.

Pellecchia [27] also examined the catalytic activity of several organometallic derivatives with similar boranes. They observed the catalytic activity of Cp^*TiMe_3 with dimethyl-

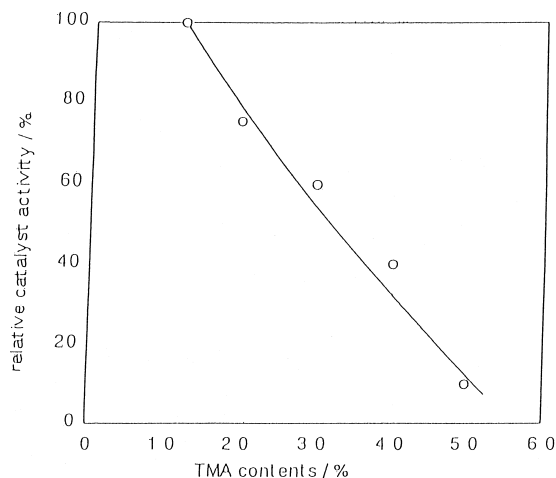


Fig. 3. Effects of trimethylaluminum in MAO on the catalyst activity.

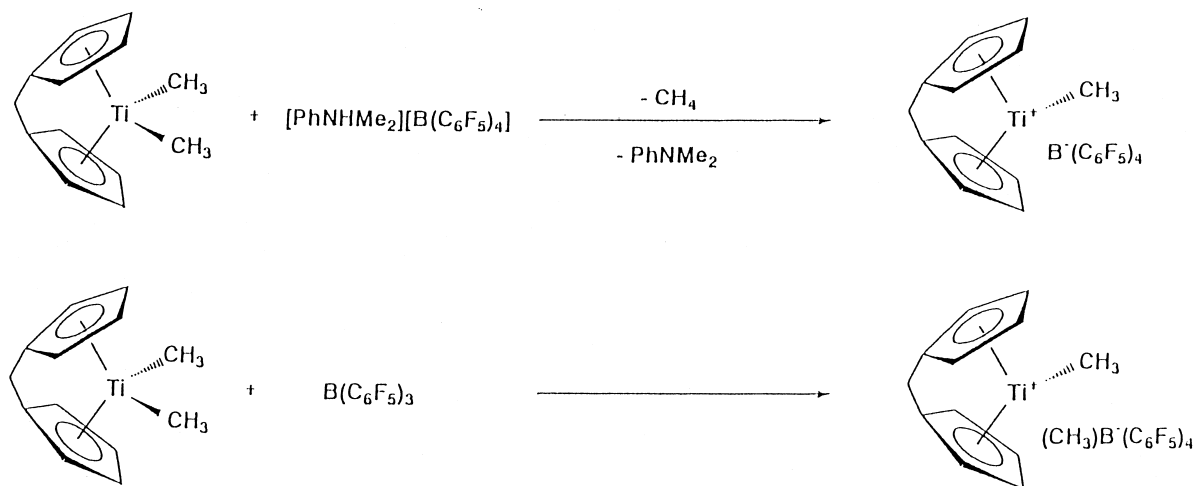


Fig. 4. Reactions between Ti compounds and boron compounds.

aniliniumtetrakis(pentafluorophenyl)borate was lower than that with tris(pentafluorophenyl)borane. They proposed free amine coordinates to the active site and interferes with the polymerization reaction.

Using the pentafluorophenyl borate with a small amount of TIBA as cocatalyst for polymerization of styrene to SPS was examined by Campbell et al. [28], Tomotsu et al. [29], and Kucht et al. [30]. TIBA was found to be the scavenger of impurities in styrene and to increase the syndiotacticity of the polymer.

2.3. Supported and heterogeneous catalyst

Mixture of highly isotactic and highly syndiotactic polystyrene were mainly obtained using heterogeneous titanium compounds such as TiCl₃, TiCl₄ supported on Mg compound [31] (Table 7).

Table 7
Polymerization of styrene using Ti compounds with MAO

Catalyst (mmol)		[Al]/[Ti]	Conversion (wt%)	Stereospecificity
TiCl ₃ (AA)	1.0	100	8.2	iso.PS + Synd.PS
	0.2	1000	2.0	iso.PS + Synd.PS
TiCl ₃ (solvay)	1.0	20	1.9	iso.PS + Synd.PS
	0.2	1000	0.9	iso.PS + Synd.PS
Mg(OEt) ₂ /EB/TiCl ₄	2.0	50	2.9	iso.PS(84) + Synd.PS(16)
	0.2	500	1.1	iso.PS(12) + Synd.PS(88)
	0.2	1000	1.4	iso.PS(10) + Synd.PS(90)
TiCl ₄	40	10	7.2	iso.PS
	5	40	0.4	iso.PS + Synd.PS
	0.2	500	0.7	Synd.PS
Ti(OEt) ₄	2	10	0.3	(Atactic PS)
	2	50	2.5	Synd.PS
	0.2	500	0.9	Synd.PS

^a[styrene] = 0.43 mol, toluene = 100 ml, 50°C, 2 h.

Table 8
Styrene polymerization with various supported catalysts [33]

Catalyst (g)	Amount of metals on SiO ₂ (mmol/g)		Polymerization conditions			Polymer yield (mg/mmolTi)	
	Ti	Al	mmol		Al/Ti	Syndio	Acta
			Ti	MAO			
Ti(OBu) ₄ 0.0340			0.10	1.0	10	30	271
Ti(OBu) ₄ 0.0340			0.10	2.0	20	860	0
Ti(OBu) ₄ 0.0340			0.10	3.0	30	716	56
Ti(OBu) ₄ 0.0340			0.10	0.5	5	47	0
Ti(OBu) ₄ /SiO ₂ 0.100	1.00		0.10	1.0	10	595	0
Ti(OBu) ₄ /SiO ₂ 0.100	1.00		0.10	2.0	20	1800	0
Ti(OBu) ₄ /SiO ₂ 0.100	1.00		0.10	3.0	30	2190	0
Ti(OBu) ₄ /SiO ₂ 0.100	1.00		0.10	4.0	40	2100	0
Ti(OBu) ₄ /MAO/SiO ₂ 0.360	0.616	16.1	0.22	5.8	26	3450	0
Ti(OBu) ₄ /MAO/SiO ₂ 0.270	0.616	11.0	0.17	3.0	18	10222	0
Ti(OBu) ₄ /MAO/SiO ₂ 0.140	0.616	14.2	0.088	2.0	23	27028	0

There would be two types of polymer arising from two different active sites. The syndiotactic polystyrene fraction increases with increasing the molar ratio of Al to Ti. The supported catalyst was washed by toluene and the catalyst performance was examined. The toluene soluble portion of the catalyst was found to produce SPS and the insoluble portion of the catalyst was found to produce IPS.

Soga et al. [32] examined SiO₂ supported Ti(OC₄H₉)₄ with MAO(Ti(OC₄H₉)₄/SiO₂ with MAO) and SiO₂ supported reacted mixture of Ti(OC₄H₉)₄ and MAO (Ti(OC₄H₉)₄/MAO/SiO₂). The syndiotacticity of the polymers with both catalysts were almost 100% (Table 8). They found catalytic activity was independent of Al/Ti molar ratio. They suggested that SiOTi(OC₄H₉)₃ heterogeneous species are more stable against reduction than the active species in the soluble system.

Al₂O₃ supported CpTiCl₃ or Cp*TiCl₃ with tri-*iso*-butylaluminum affords mixtures of IPS and SPS [33]. Two possible initiating sites are thought to be present on the catalyst surface. The first one is formed by the reaction of CpTiCl₃ with surface hydroxyl groups of Al₂O₃ and is responsible for isospecific polymerization [34]. The second one is formed by the reaction of CpTiCl₃ with Lewis acid sites and is responsible for syndiospecific polymerization.

3. The mechanisms for stereochemical control in syndiotactic polymerization of styrene

Catalysts for the syndiospecific polymerization of styrene are typically Group IV metal compounds, especially titanium compounds, with MAO or borate derivatives as the cocatalyst [7,28,29,64–77]. Several studies have been carried out to clarify the nature of the active center and to explain the mechanisms of polymerization and of stereochemical control.

3.1. The mode of addition of the growing polymer chain to the double bond of the monomer

It is known that both isotactic and syndiotactic polymerization of propylene with Ziegler–Natta catalysts occurs by the *cis*-opening of the double-bond [35]. A syndiotactic polymer can be described as a sequence of mirror-related syndiotactic diads (Fig. 5).

Scheme 1 shows the relationship between two kinds of copolymers obtained from deuterium substituted styrene monomer and the conformation of their vicinal protons. As shown in Scheme 1,

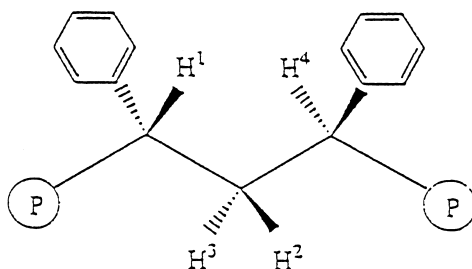
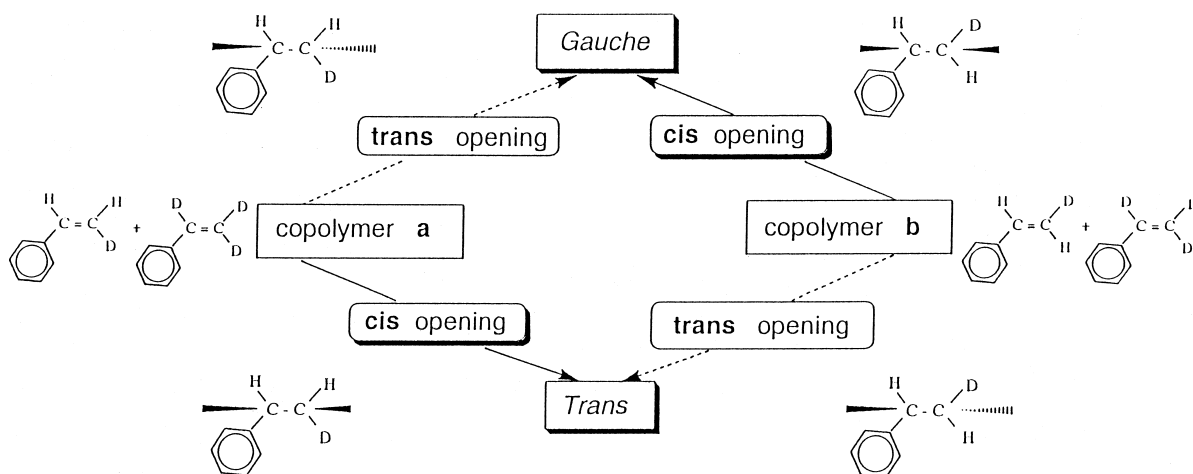


Fig. 5. The sequence of mirror-related syndiotactic polystyrene diads.

cis opening polymerization should give a *trans* conformation for the copolymer (a), as was obtained from the copolymerization of *cis*- β -d₁-styrene and α,β,β -d₃-styrene, and a *gauche* conformation for the copolymer (b), as was obtained from copolymerization of *trans* β -d₁-styrene and α,β,β -d₃-styrene. In contrast, when *trans* opening occurs in copolymerization, we should observe a *gauche* conformation for copolymer (a) and a *trans* conformation for copolymer (b). The catalyst system used for the syndiotactic polymerization was CpTiCl₃/MAO. Two type of copolymers were prepared. Copolymer (a) was prepared with *cis*- β -d₁-styrene (15 mol%) and α,β,β -d₃-styrene (85 mol%). Copolymer (b) was prepared with *trans*- β -d₁-styrene (15 mol%) and α,β,β -d₃-styrene (85 mol%). Fig. 6 shows the phenyl C₁ resonances of copolymers (a) and (b). The very sharp signals at $\delta = 145.10$ ppm are assigned to the racemic pentad (*rrrr*) configuration. The syndiotacticity, directly measured from the relative peak areas, were 85% and 80%, respectively, showing that these copolymers have a high degree of stereoregularity. The ¹H-NMR spectra of the copolymers (a) and (b) have been determined and the resonances are assignable to the methine and methylene protons in the main chain region as shown in Fig. 7. The NMR data are summarized in Table 9.

According to Zambelli [35], the main chain of the syndiotactic polymer has a statistically *trans*–*trans* conformation. Others have also reported X-ray diffraction measurements which show that SPS crystallizes in a planar zig-zag (*trans*–*trans*) conformation and consequently the dihedral angle between the two vicinal protons must be *trans* (180°) or *gauche* (60°).

According to Karplus [36,78], the $J_{\text{H-H}}$ coupling constant of a *trans* conformation is larger than



Scheme 1. The relation between two kinds of deuterated polymers and the conformation of the vicinal protons [15]. (a) *cis*- β -d₁-St/ α,β,β -d₃-St, (b) *trans*- β -d₁-St/ α,β,β -d₃-St.

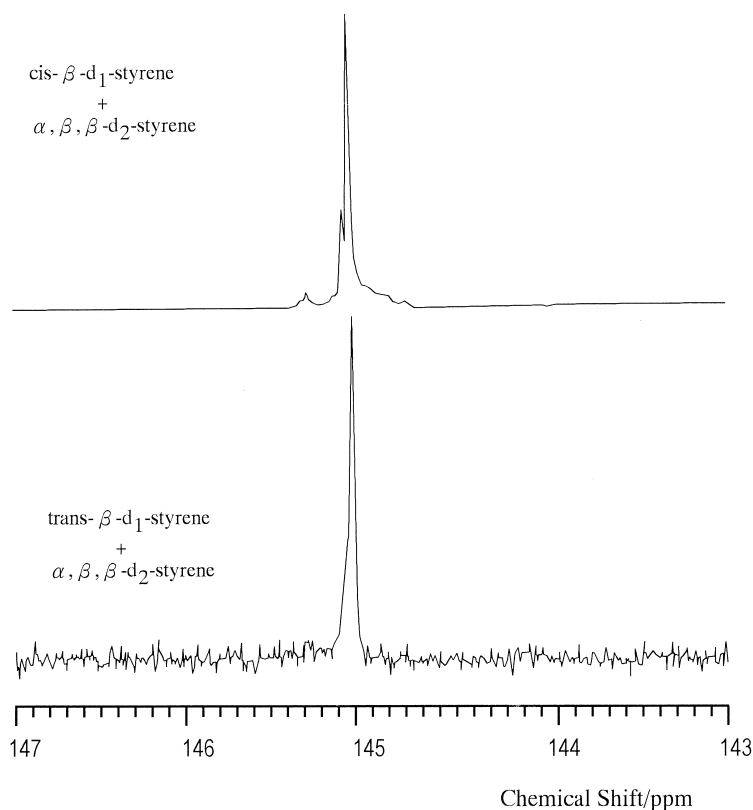


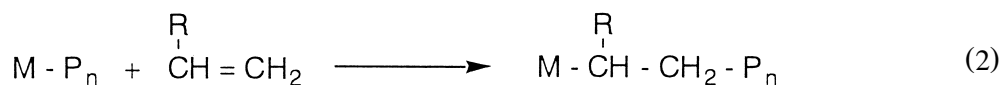
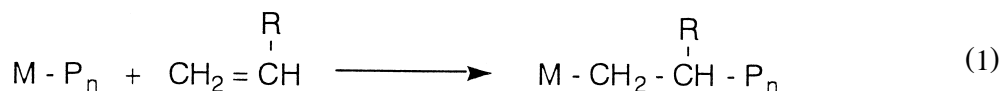
Fig. 6. 100 MHz ^{13}C -NMR spectra of phenyl C_1 region of the copolymer (a) and copolymer (b).

that of a gauche one. The ^1H -NMR spectra show that the coupling constant of copolymer (a) is larger than that of copolymer (b). Therefore, copolymer (a) has a *trans* ($J_t = 9.28$ Hz) conformation and copolymer (b) is gauche ($J_g = 5.37$ Hz). Independently, Longo et al. [37] also observed a *trans* ($J_t = 9.0$ Hz) conformation from a copolymer of type (a), which they obtained using the tetrabenzyltitanium/MAO catalyst system.

It was concluded that the double-bond opening mechanism in syndiotactic specific polymerizations of styrene is *cis* opening. This is the same opening mechanism as for the syndiotactic specific polymerization of propylene using the $\text{VCl}_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ catalyst system at low temperatures [38].

3.2. Stereochemistry of the styrene insertion

The regiochemistry of the insertion can in principle proceed in two ways, either primary (Eq. (1)) or secondary (Eq. (2)).



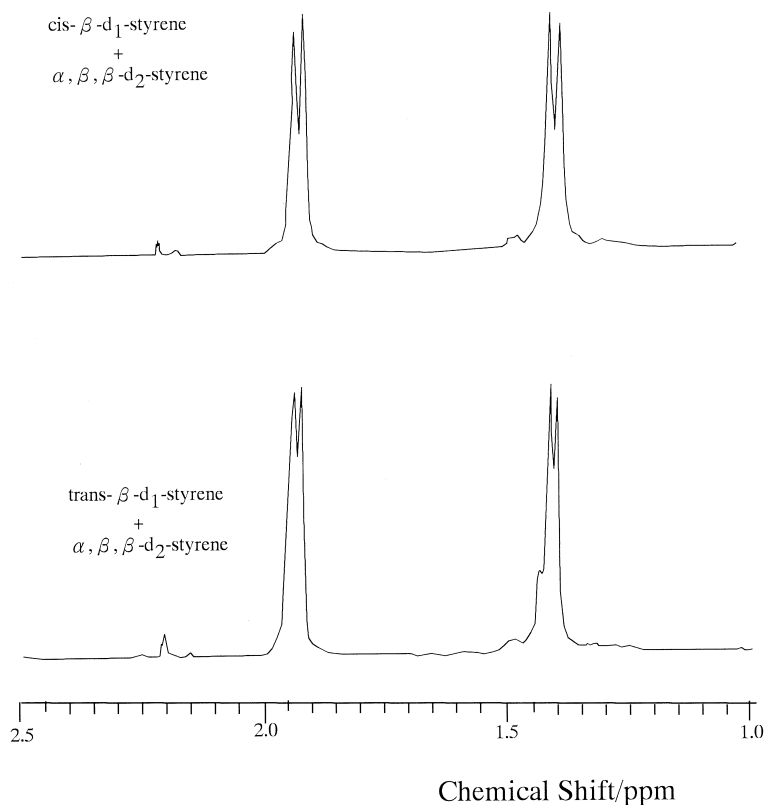


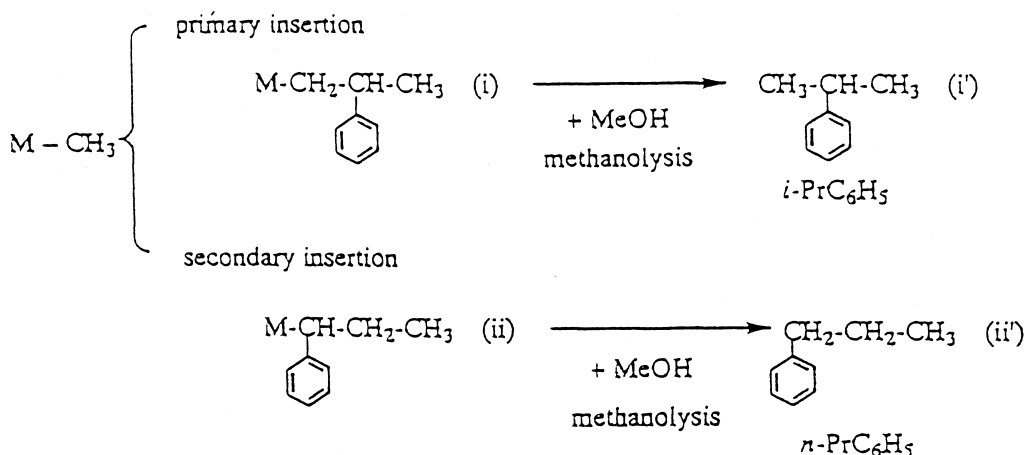
Fig. 7. 400 MHz ^1H -NMR spectra of methine and methylene of the copolymer (a) and copolymer (b).

With isospecific Ziegler–Natta catalysts it has been shown that the polymerization of propylene and higher α -olefins proceed by primary insertion with occasional errors [39,79–82]. Secondary insertion prevails in the propagation step of propylene with syndiospecific catalysts [40,83–85]. However, attempts to synthesize syndiotactic polymers of higher 1-alkyl substituted olefins has not yet been achieved and it is believed that the secondary insertion of higher 1-alkyl substituted olefins into the stereospecific catalytic site is prevented for steric reasons.

Styrene, because of its aromatic character, behaves differently from an alkyl-olefin with respect to its polymerization reaction. The objective of the work described below was to characterize the stereochemistry of styrene insertion into the carbon–metal bond of a soluble syndiospecific Ziegler–Natta catalyst. It is generally agreed that the mechanism of syndiospecific polymerization of styrene is metal-coordinated.

Table 9
The chemical shifts and coupling constants of copolymer (a) and copolymer (b)

Copolymer	Chemical shifts (ppm)		Coupling constant (Hz)
	methylene	methine	
Copolymer (a)	1.40	1.94	9.28
Copolymer (b)	1.41	1.94	5.37

Scheme 2. Possible addition modes of a styrene molecule to a metal- CH_2 bond.

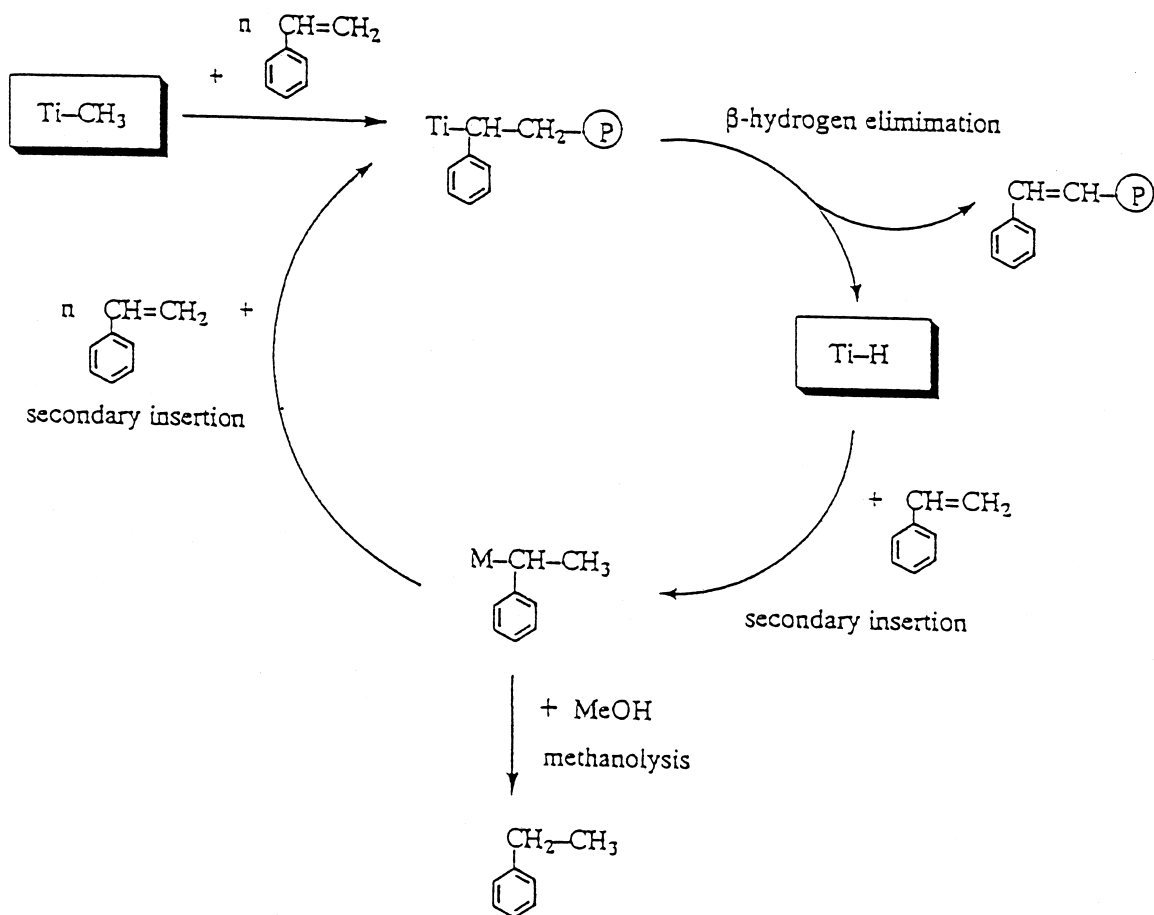
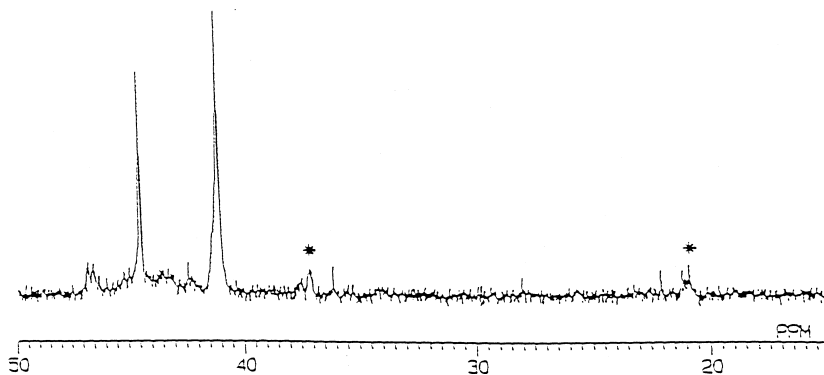
The possible insertion process for styrene into a metal–methyl bond, which is presumed to arise from methylation of the titanium by MAO in syndiospecific catalyst systems, may be formulated as primary insertion (i) or secondary insertion (ii) shown in Scheme 2. *n*-Propylbenzene (*n*-PrC₆H₅) was the product after methanolysis of the syndiospecific polymerization reaction mixture [10]. Therefore, it was concluded that the insertion of styrene into the Ti–CH₃ bond proceeds by a secondary (2,1 addition) process. The results also show, in addition, that ethylbenzene (EtC₆H₅) was formed after methanolysis of the catalytic reaction. The ethylbenzene arises via secondary insertion into a titanium hydride formed from β -hydride elimination of the growing polymer chains, according to Scheme 3.

On the other hand, the ¹³C-NMR spectrum (Fig. 8) of the low molecular weight SPS formed in the reaction shows additional resonances in the region of the saturated carbons at $d = 37.0$ and 21.0 ppm. These resonances can be attributed to C(1), C(2), of C(1)H(C₆H₆)C(2)H₃.

We propose that these groups arise from reinitiation via secondary insertion on the M–H bonds which would give the observed 1-phenylethyl end groups. These end groups could arise also from primary insertion into M–CH₃ bonds, but this possibility can be disregarded, since a secondary insertion has been observed by gas chromatography, and there is no evidence (NMR) for head–head arranged monomer units. Furthermore, it is observed that the amount of ethylbenzene is larger than that of *n*-PrC₆H₅. This fact suggests polymer chains are mainly initiated via M–H bonds and terminated by β -hydride elimination.

In confirmation of this active site analysis work, Zambelli et al. [41,86] independently studied the stereochemistry of styrene insertion catalyzed by Ti(benzyl)₄/MAO system. The ¹³C-NMR spectrum of the polymer obtained showed that the chain end of the polymer was consistent with a secondary insertion mechanism both in the initiation steps and in the propagation steps even when the former occurs via M–H bond. They also showed that most of the polymer chains was initiated by M–H bonds.

Newman and Malanga [42] examined the characteristic backbone error of syndiotactic styrene polymerization to differentiate chain-end control over site control mechanism. The syndiotacticity of polymer produced by CpTi(OMe)₃/MAO system was lower than that of Cp*Ti(OMe)₃, especially at higher polymerization temperatures. Both of catalyst made rrmr type errors and a lack of rmmr pentads. This results shows that the steric effects of the Cp ligands increase the stereoselectivity and the mechanism of SPS proceeds via a chain end control.

Scheme 3. The formation of ethylbenzene arising from β -hydrogen elimination.Fig. 8. 75.5 MHz ^{13}C -NMR spectrum in CDCl_3 of the low molecular weight SPS.

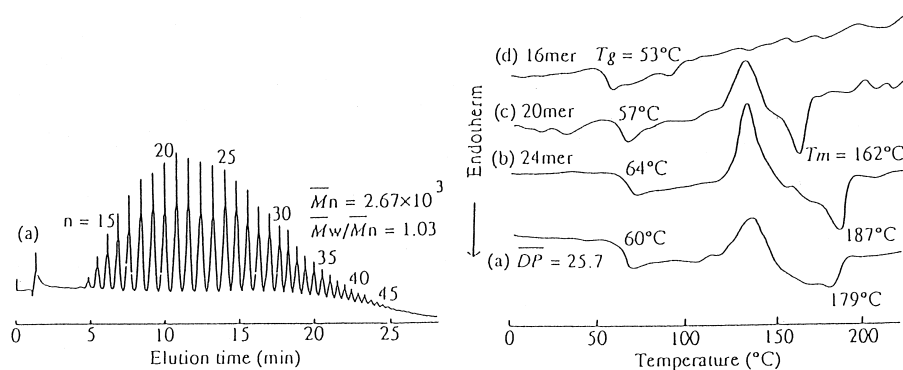


Fig. 9. SFC curve and DSC curves of SPS.

Ute et al. [43] examined the supercritical fluid chromatography of the polymer made by CpTiCl_3 with MAO. They separated polymer by the molecular weight (Fig. 9). The end groups of the polymer were $-\text{CH}=\text{CHPh}$ and $\text{CH}_3-\text{CHPh}-$. They concluded that polymerization proceeds via insertion of the monomer to the Ti–H bond and β -hydride elimination must occur. They also observed there were many mistakes in stereoregularity in the low molecular weight SPS.

The addition of hydrogen may increase the amount of Ti–H which is the initial structure of active site. The effects of hydrogen on catalytic activity was examined by Tomotsu et al. [14]. The data are shown in Table 10. The addition of hydrogen increases catalytic activity and these results support the hypothesis that polymerization proceeds via a Ti–H complex. A generalized polymerization mechanism is shown in Fig. 10.

3.3. Active species

The nature and formation of the true active catalytic species are not yet fully elucidated. In polymerization of α -olefins, it is generally accepted that homogeneous catalysts based on Group IV metallocenes with MAO consist of cationic complexes.

Newman and Malanga have synthesized the titanium(III) metallocene, $\text{Cp}^* \text{Ti}(\text{OMe})_2$, via reduction of $\text{Cp}^* \text{Ti}(\text{OMe})_3$ with *t*-butyllithium and characterized the complex via X-ray crystallography [44]. The complex is dimeric with two bridging methoxide groups, two terminal methoxide groups and two Cp^* rings *trans* to each other with respect to the Ti–Ti. The two halves of the dimer are related by a 2-fold symmetry axis. Table 11 shows a comparison of the percent conversion for $\text{Cp}^* \text{Ti}(\text{OMe})_2$ and $\text{Cp}^* \text{Ti}(\text{OMe})_3$ with varying MAO ratio in the MAO activated system. At very

Table 10
Effects of hydrogen on polymerization

Hydrogen pressure	Relative activity ^a
none	100
0.1	160
0.5	210
1.0	220

^aCatalytic activity without hydrogen as 100.

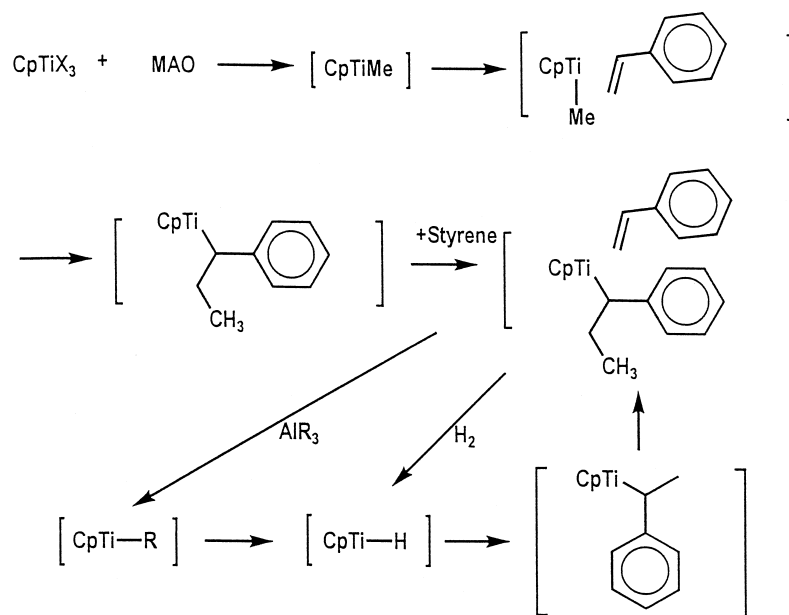


Fig. 10. Proposed polymerization mechanism.

low MAO ratio, both catalysts yield very little SPS. However, $\text{Cp}^* \text{Ti}(\text{OMe})_2$ gives a higher conversion at lower MAO ratio than $\text{Cp}^* \text{Ti}(\text{OMe})_3$. Table 12 shows a comparison of percent conversion for $\text{Cp}^* \text{Ti}(\text{OMe})_2$ and $\text{Cp}^* \text{Ti}(\text{OMe})_3$ with the addition of tri-*iso*-butylaluminum (TIBA) in the MAO cocatalyst system. The trend of increasing conversion with TIBA content is observed in Table 12 for $\text{Cp}^* \text{Ti}(\text{OMe})_3$ and relatively low conversion is observed with no TIBA. However, for $\text{Cp}^* \text{Ti}(\text{OMe})_2$, high conversion is obtained even with no TIBA and the conversion is higher than for $\text{Cp}^* \text{Ti}(\text{OMe})_3$. This suggests the function of the aluminum alkyl is reduction of the Ti(IV) species while the MAO cocatalyst generates the active Ti(III) cationic site. Thus, the Ti(III) complex requires less aluminum alkyl overall, i.e., less MAO and no TIBA.

The effect of the molar ratio of MAO to Ti on the catalytic activity in the case of CpTiCl_3 with a MAO catalyst system was investigated [45]. The activity increases with an increasing molar ratio of MAO to Ti. The amount of cationic Ti(III) species measured by ESR increases with increasing ratio

Table 11

Percent conversion to SPS with MAO content. Molar ratios styrene:MAO:Ti 233,333:MAO:1; 70°C for 1 h

Catalyst	MAO-Ti	Conversion (%)
$\text{Cp}^* \text{Ti}(\text{OMe})_2$	25	10
	50	32
	100	55
	200	63
$\text{Cp}^* \text{Ti}(\text{OMe})_3$	25	2
	50	22
	100	33
	200	41

Table 12

Percent conversion to SPS with TIBA content. Molar ratios styrene:MAO:TIBA:Ti 233,333:200:TIBA:1: 70°C for 1 h

Catalyst	TIBA:Ti	Conversion (%)
Cp* Ti(OMe) ₂	0	58
	6	62
	10	64
	50	66
Cp* Ti(OMe) ₃	0	30
	6	47
	10	53
	50	62

of MAO to Ti as well. This suggests that MAO acts as a reducing agent for Ti(IV) to Ti(III). Cationic Ti(III) might be an active species for synthesis of SPS. Some evidence reported in the literature suggests that the active species promoting syndiotactic polymerization of styrene is a cationic Ti(III) complex bearing a η^5 anionic ligand (Cp or Cp*) and the growing polymer chain [46]. Chien et al. [47] asserted that the titanium oxidation state for active catalytic species was Ti(III) both in CpTiX₃/MAO and in TiX₄/MAO. They found that in Ti(CH₂C₆H₅)₄/MAO system titanium had a distribution of oxidation states, with Ti(IV):Ti(III):Ti(II) about 53:27:20. The addition of styrene caused a change in this ratio to 36:48:16. The ESR spectra are also consistent with the almost quantitative formation of such hydrotitanium (III) complexes.

Analogous studies were carried out by Zucchini et al. [48]. They found that in the absence of styrene, titanium had mainly a III oxidation state. ESR measurements revealed the formation of an unidentified new Ti(III) species, possibly containing a Ti–H bond, suggesting a certain degree of β -hydrogen abstraction of the bonded polymer.

Titanium compounds are most likely reduced before the active site formation. Alkylmetal compounds are both alkylating and reducing reagents for titanium. The effects of reductants on the catalytic activity were evaluated and the data are summarized in Table 13 [14]. Very strong reduction reagents like Al(CH₃)₃, Al(C₃H₅)₃ reduce the catalytic activity. In this case, the titanium compound may be reduced to Ti(II) or Ti(I) by these reagents. But the catalytic activity is increased by the addition of TIBA. The details of the effects of TIBA were evaluated and are shown in Fig. 11 [14]. TIBA increases the catalytic activity and reduces the molecular weight of the polymer. TIBA most

Table 13

Polymerization activity of [Me₃Cp]TiCl₃ with MAO and an alkylation reagent

Reagent	Relative activity ^a	M _w
None	100	750 000
Al(CH ₃) ₃	13	64 000
Al(C ₂ H ₅) ₃	23	84 000
Al(<i>n</i> -C ₄ H ₉) ₃	76	570 000
Al(<i>i</i> -C ₄ H ₉) ₃	560	580 000
Al(<i>n</i> -C ₈ H ₁₇) ₃	100	670 000
Al(C ₂ H ₅) ₂ (OC ₂ H ₅)	140	870 000
Zn(C ₂ H ₅) ₂	48	130 000

^aCatalyst activity without alkylation reagent as 100, polymerization temperature 700°C.

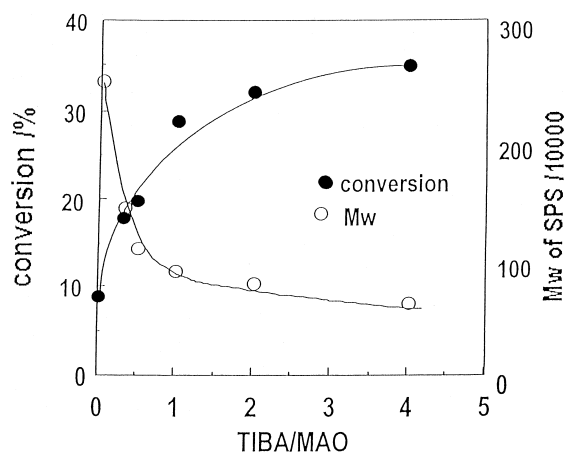


Fig. 11. Effects of TIBA on the catalyst activity of $\text{Cp}^*\text{Ti}(\text{OMe})_3$ with MAO.

likely reacts with the titanium compound to reduce it from Ti(IV) to Ti(III). Moreover, TIBA reacts with metal alkyl bonds and, therefore, acts as a chain transfer reagent during polymerization.

4. Polymerization of substituted styrene and copolymerization of styrene and ethylene

4.1. Polymerization of substituted styrene

When various ring-substituted styrenes were polymerized using the CpTiCl_3 and MAO catalyst system, the corresponding syndiotactic polystyrenes were obtained. The ^{13}C -NMR spectra of the phenyl C_1 carbon for the poly(ring-substituted) styrene show, in each case, a sharp resonance at a high magnetic field (Fig. 12(3)). These spectra are similar to that of syndiotactic PS. In poly(*p*-fluorostyrene), the peak at high magnetic field is split, due to coupling to the ^{19}F nucleus. These results show that these polymers are highly syndiotactic. For comparison, the spectra of each atactic poly(ring-substituted) styrene (Fig. 12(1)) show many main peaks corresponding to their various configurational sequences. These spectra are similar to that of atactic PS. The spectra of each isotactic poly(ring-substituted) styrene (Fig. 12(2)) shows a single sharp peak at a lower magnetic field corresponding to the mmmm pentad configuration. These spectra are similar to that of isotactic PS.

Recently, Zambelli et al. [49] succeeded in obtaining syndiotactic poly(*p*-methylstyrene) and poly(*m*-methylstyrene) but could not succeed in the preparation of syndiotactic poly(*p*-chlorostyrene) and poly(*m*-chlorostyrene) using the $\text{Ti}(\text{benzyl})_4/\text{MAO}$ system. The difference of the results might be caused by the difference in the catalyst system.

Fig. 13 shows the relation between the Hammett's σ value of each substituent and reactivities in polymerization. It is observed that monomer reactivity is enhanced by electron-releasing substituents in an aromatic ring. Even when *p*-*tert*-butylstyrene, a substituent of large steric hindrance, shows a high reactivity. This indicates that there is a strong polar effect of the substituent on the rate of addition. Soga et al. [50] examined the copolymerization of styrene and substituted styrene and calculated the reactivity ratios for styrene and ring substituted styrene (Fig. 14). Their result also suggests that the reactivity is enhanced by electron-releasing substituents in an aromatic ring.

Natta et al. [51] previously reported a comprehensive investigation concerning the reactivity of substituted styrenes in the presence of heterogeneous isospecific catalyst systems. Electron-releasing

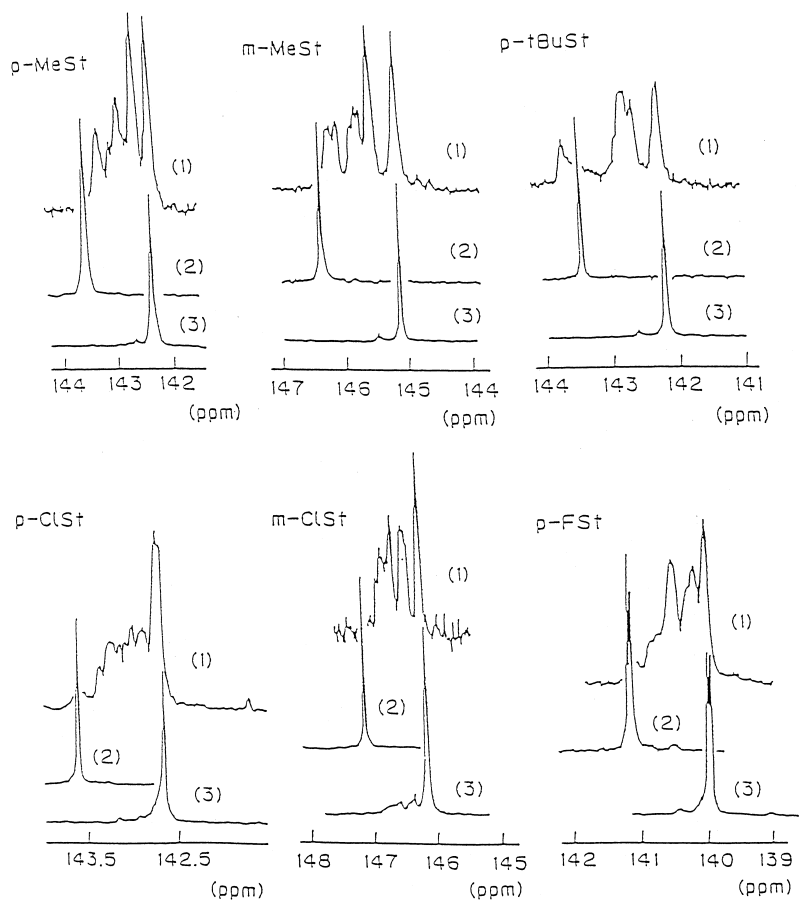


Fig. 12. 67.8 MHz ^{13}C -NMR spectra of poly(substituted styrene): (1) atactic, (2) isotactic, and (3) syndiotactic.

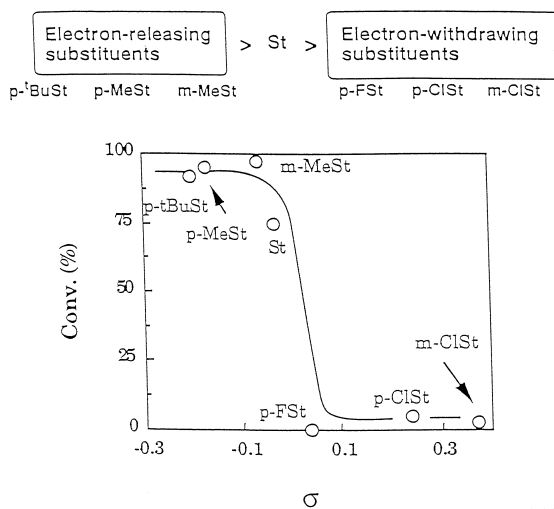


Fig. 13. Relationship between the Hammett σ value of substituted styrenes and polymerization rate.

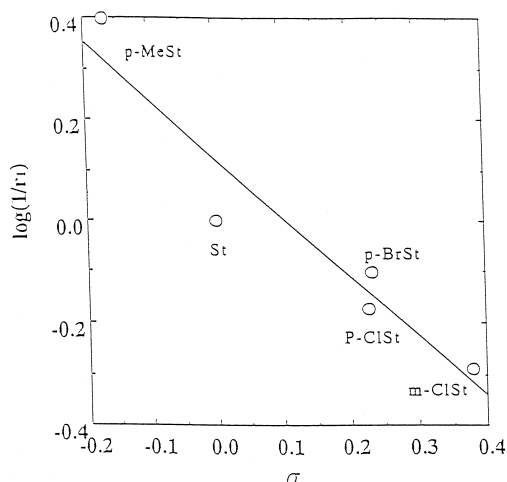


Fig. 14. Relationship between the Hammett σ value of substituted styrenes and reactivity ratio of copolymerization.

substituents on the aromatic ring increased the reactivity of the monomers while electron-withdrawing substituents had a deactivating effect. Halogenated styrenes give stereoregular homopolymers according to the authors, while stereoregularity is very poor or absent according to Zambelli and Soga. In this isospecific polymerization, the mode of monomer insertion is primary [52,87]. These results indicate that anionic coordinative polymerization is the mechanism for this polymerization.

On the other hand, in syndiospecific polymerization of styrene, the monomer addition is secondary. In addition, monomer reactivity is enhanced by electron-releasing substituents in the aromatic ring. The electronic effect of the substituent of the ring is transmitted more efficiently to a methine than to methylene carbon. These results may also suggest that the aromatic ring of either the monomer or the last unit of the growing chain could be involved in the coordination to the catalyst in order to ensure the syndiotactic steric control. The presence of electron-attracting substituents should greatly reduce the coordination of the monomer and of the aromatic ring of the last unit of the growing chain end and, consequently, the stereoregularity of insertion. In fact, Soga et al. examined copolymerization of

Table 14
 T_g and T_m of syndiotactic and isotactic polystyrene derivatives

Monomer ^a	Stereospecificity			
	syndiotactic		isotactic	
	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
St	100	266	99	224
<i>m</i> -MeSt	72	206	71	125
<i>p</i> -MeSt	106	173	101	—
<i>p</i> - ^t BuSt	137	310	125	308
<i>m</i> -FSt	86	275		
<i>p</i> -FSt	94	322	101	247
<i>m</i> -ClSt	85	192	84	124
<i>p</i> -ClSt	124	299	124	165
<i>p</i> -BrSt	131	—		

^aSt = styrene, *m*-MeSt = *m*-methylstyrene, *p*-MeSt = *p*-methylstyrene, *p*-^tBuSt = *p*-*tert*-butylstyrene, *m*-FSt = *m*-fluorostyrene, *p*-FSt = *p*-fluorostyrene, *m*-ClSt = *m*-chlorostyrene, *p*-ClSt = *p*-chlorostyrene, *p*-BrSt = *p*-bromostyrene.

styrene and indene [53] and suggested that the syndiotactic polymerization of styrene does not proceed via a coordinated-anionic mechanism but via a coordinated-cationic mechanism.

The melting point of syndiotactic poly(ring-substituted) styrene and the corresponding isotactic polymer are given in Table 14. Almost all the syndiotactic polymers produced have a high degree of crystallinity, and all the T_m values of syndiotactic polymers are higher than those of isotactic polymers with the corresponding substituent.

4.2. Copolymerization of styrene and ethylene

Mani et al. [54] examined the copolymerization of ethylene and styrene by using $TiCl_3$ with MAO. Because they used the heterogeneous catalyst, the polymer obtained was isotactic polystyrene with some evidence of ethylene styrene copolymer formation. The first trial of styrene and ethylene copolymerization by homogeneous catalyst for syndiospecific polymerization of styrene was examined by Tazaki et al. [55]. They obtained copolymer which had small amount of ethylene unit in the polymer from ethylene and styrene using monocyclopentadienyl or tetraalkoxy titanium compounds with MAO. Longo et al. [56] examined styrene ethylene copolymerization with the catalyst system $CpTiCl_3$ with MAO. They found MAO/Ti ratio affected the performance of copolymerization. The catalyst system with MAO/Ti ratio of 1000 produced block copolymer, while with a ratio of 100

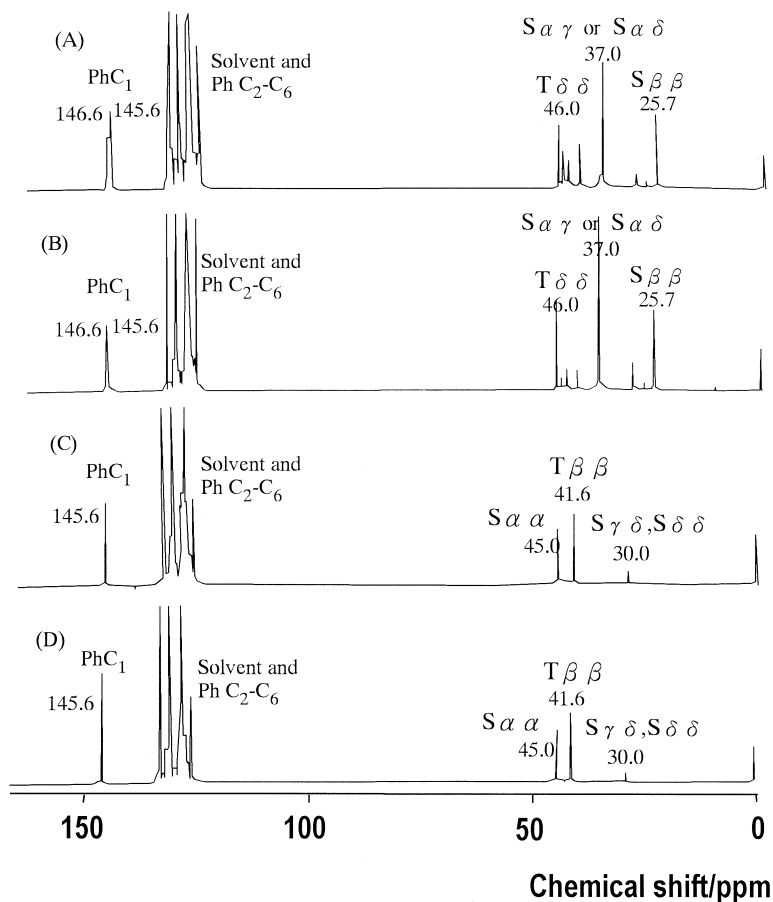


Fig. 15. ^{13}C -NMR spectra of ethylene styrene copolymers prepared with: (A) $(TBP)Ti(Oi-Pr)_2/MAO$, (B) $(TBP)TiCl_2/MAO$, (C) $(MBP)TiCl_2/MAO$, (D) $(TBP)Ti(Oi-Pr)_2/MAO$.

polyethylene bridged by styrene was produced. On the other hand, Seppala et al. [57,88] also examined the copolymerization of styrene and ethylene by titanium compounds with bulky alkoxy ligands and also CpTiCl_3 with MAO. The products of the polymerization were a mixture of polyethylene and syndiotactic polystyrene. They proposed there are more than two active sites in this catalyst system.

Xu et al. analyzed the products of ethylene styrene copolymerization with $\text{CpTi}(\text{OPh})_3$ and MAO [58]. They found this polymer was elastoplastic and amorphous copolymer. They also found external addition of trimethylaluminum or tri-*iso*-butylaluminum promoted styrene homopolymerization. They analyzed the catalyst by ESR spectroscopic analysis and concluded a cationic titanium Ti(IV) complex produced polyethylene and a Ti(III) complex produced syndiotactic polystyrene. Styrene ethylene copolymerization was proceeded via a third intermediate complex.

Pellecchia et al. [59] examined $\text{Ti}(\text{benzyl})_4$ with borane for producing ethylene styrene copolymer. They reported that all sequences showed alternating copolymer. Inoue et al. [60] examined zirconium complexes for ethylene-styrene copolymerization. They found alternating copolymer and homopolymer. The stereoregularity of polymer was atactic.

Kakugo et al. [61] reported that a catalyst based on 2,2'-thiobis(4-methyl-6-*tert*-butylphenoxy)titanium dichloride, $(\text{TBP})\text{TiCl}_2$, and MAO produced a mixture of syndiotactic polystyrene and the alternating ethylene–styrene copolymer (Fig. 15). The authors stressed the role of sulfur as essential to obtain the alternating copolymer, since the copolymer was not produced by using a similar compound having a CH_2 bridge (2,2'-methylenebis(4-methyl-6-*tert*-butylphenoxy)titanium dichloride, $(\text{MBP})\text{TiCl}_2$) instead of a S bridge as catalyst ligand. Subsequently, a patent [62] disclosed the ethylene styrene copolymerization promoted by catalysts based on bridged amido-monocyclopentadienyl titanium complexes, such as [dimethylsilyl(phenylamido)(Cp^*)]titanium dichloride and MAO. The copolymer obtained was a random copolymer which did not contain any regioregularity in the arrangement of the styrene–styrene sequences. Oliva et al. found the similar polymer was produced with ethylenebis(1-indenyl)zirconium dichloride with MAO at -25°C [63].

5. Concluding remarks

The discovery of homogeneous metallocene catalysts in the 1980s has opened up new possibilities to fine-tune the stereochemical structure of polymer products. Using these novel catalysts, a large number of novel polymers with specific properties have been obtained. The development of these catalysts for commercial processes and commercial polymers will be a dominant force in the polymer industry through the next century.

References

- [1] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* 18 (1980) 99.
- [2] J. Boor Jr., *Ziegler–Natta Catalyst and Polymerization*, Academic Press, New York, 1979.
- [3] J.C.W. Chien, *Coordination Polymerization*, Academic Press, New York, 1975.
- [4] G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, M. Peraldo, *Chim. Ind.* 38 (1956) 124.
- [5] G. Natta, F. Danusso, D. Sianesi, *Makromol. Chem.* 28 (1958) 253.
- [6] F. Danusso, D. Sianesi, *Chim. Ind.* 40 (1958) 450.
- [7] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Polym. Prepr. Jpn.* 35 (1986) 240.
- [8] A. Zambelli, L. Oliva, C. Pellecchia, *Macromolecules* 22 (1989) 2129.
- [9] P. Longo, A. Grassi, L. Oliva, P. Ammendola, *Makromol. Chem.* 191 (1990) 237.
- [10] N. Ishihara, D. Phill. Thesis, Oxford, 1990.

- [11] R.E. Campbell, M.T. Malanga, *Metcon* 93 (1993) 315.
- [12] W. Kaminsky, *Metallocenes* 96 (1996) 211.
- [13] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, *Macromolecules* 26 (1993) 5822.
- [14] N. Tomotsu, M. Kuramoto, M. Takeuchi, H. Maezawa, *Metallocenes* 96 (1996) 211.
- [15] J.C.W. Chien, *Metallocenes* 96 (1996) 223.
- [16] A. Miyashita, M. Mabika, T. Suzuki, *Proc. Int. Symposium on Synthetic, Structural and Industrial Aspects of Stereospecific Polymerization*, Milano, Italy, 1994.
- [17] N. Ishihara, M. Kuramoto, *Stud. Surf. Sci. Catal.* 89 (1994) 339.
- [18] M.L.H. Green, N. Ishihara, *J. Chem. Soc. Dalton Trans.* (1994) 657.
- [19] C. Pellecchia, P. Longo, A. Grassi, P. Ammendola, A. Zambelli, *Makromol. Chem. Rapid Commun.* 8 (1987) 227.
- [20] P. Longo, A. Proto, L. Oliva, *Makromol. Chem. Rapid Commun.* 15 (1994) 151.
- [21] M. Yang, C. Cha, Z. Shen, *Polym. J.* 22 (1990) 919.
- [22] A. Miyashita, *Polym. Preprints Jpn.* 42 (1993) 2295.
- [23] A. Miyashita, M. Nabika, T. Suzuki, 40th Japanese Symposium on Organometallic Chemistry, abstract, 1993, pp. 46.
- [24] N. Tomotsu, *Polymer Preprints Japan* 2 (1993) 226.
- [25] A. Miyashita, M. Nabika, T. Suzuki, 41st Japanese Symposium on Organometallic Chemistry, abstract, 1994, p. 46.
- [26] R. Quyoum, Q. Wang, M. Tudoret, M. Baird, *J. Am. Chem. Soc.* 116 (1994) 6435.
- [27] C. Pellecchia, P. Longo, A. Proto, A. Zambelli, *Macromol. Chem. Rapid Commun.* 13 (1992) 265.
- [28] R.E. Campbell, US Patent 5066741.
- [29] N. Tomotsu, Japanese Patent 2415574.
- [30] H. Kucht, A. Kucht, J.C.W. Chien, M.D. Rausch, *Appl. Organomet. Chem.* 4 (1994) 393.
- [31] K. Soga, T. Monoi, *Macromolecules* 23 (1990) 1560.
- [32] K. Soga, H. Nakatani, *Macromolecules* 23 (1990) 957.
- [33] K. Soga, R. Koide, T. Uozumi, *Macromol. Chem. Rapid Commun.* 14 (1993) 511.
- [34] K. Soga, T. Uozumi, H. Yanagihara, T. Shiono, *Macromol. Chem. Rapid Commun.* 11 (1990) 229.
- [35] A. Zambelli, M. Giongo, G. Natta, *Macromol. Chem.* 112 (1968) 183.
- [36] M. Karplus, *J. Chem. Phys.* 30 (1959) 11.
- [37] P. Longo, A. Grassi, A. Proto, P. Ammendola, *Macromolecules* 21 (1988) 24.
- [38] Y. Doi, S. Ueki, S. Tamura, S. Nagahara, T. Keii, *Polymer* 23 (1982) 258.
- [39] P. Longi, G. Mazzanti, A. Roggero, A.M. Lachi, *Makromol. Chem.* 61 (1963) 63.
- [40] T. Takegami, T. Suzuki, *Bull. Chem. Soc. Jpn.* 42 (1969) 848.
- [41] A. Zambelli, P. Longo, C. Pellecchia, A. Grassi, *Macromolecules* 20 (1987) 649.
- [42] T.H. Newman, M.T. Malanga, *Proc. 4th SPSJ Int. Polymer Conf.*, 1 December 1992, Yokohama, p. 27.
- [43] K. Ute, T. Takahashi, K. Hatada, *Polymer Preprints Jpn.* 43 (1994) 168.
- [44] T.H. Newman, M.T. Malanga, *J. Macromol. Sci.* (1997) in press.
- [45] N. Ishihara, M. Kuramoto, in: *Catalyst Design for Tailor-made Olefins*, Soga, K. and Terano, M. (Eds.), Kodan-sha, 1994.
- [46] A. Zambelli, C. Pellecchia, L. Oliva, P. Longo, A. Grassi, *Makromol. Chem.* 192 (1991) 223.
- [47] J.C.W. Chien, Z. Salaika, S. Dong, *Macromolecules* 25 (1992) 3199.
- [48] T. Dall'occo, F. Sartori, G. Vecellio, U. Zucchini, *Makromol. Chem.* 192 (1991) 223.
- [49] A. Grassi, P. Longo, A. Proto, A. Zambelli, *Macromolecules* 22 (1989) 104.
- [50] T. Monoi, H. Nakatani, K. Soga, *Polym. Preprints Jpn.* 38 (1989) 1726.
- [51] G. Natta, F. Danusso, D. Sianesi, *Makromol. Chem.* 31 (1959) 238.
- [52] P. Longi, G. Mazzanti, A. Roggero, M.P. Lachi, *Makromol. Chem.* 61 (1963) 63.
- [53] K. Soga, T. Monoi, *Macromolecules* 22 (1989) 3824.
- [54] R. Mani, C.M. Burns, *Macromolecules* 24 (1991) 5476.
- [55] T. Tazaki, Japanese Patent 2059871, 3087301.
- [56] P. Longo, A. Grassi, L. Oliva, *Makromol. Chem.* 191 (1990) 2387.
- [57] P. Aaltonen, J. Seppala, L. Matilainen, M. Leskela, *Macromolecules* 27 (1994) 3136.
- [58] G. Xu, S. Lin, *Macromolecules* 30 (1997) 685.
- [59] C. Pellecchia, D. Pappalardo, M. D'Arco, A. Zambelli, *Macromolecules* 29 (1996) 1158.
- [60] N. Inoue, T. Shiomura, *Polym. Preprints Jpn.* 42 (1993) 2292.
- [61] M. Kakugi, T. Miyatake, K. Mizunuma, *Catalytic Olefin Polymerization*, Elsevier Science B.V., Amsterdam, 1990, p. 517.
- [62] C. Stevens, European Patent 416815A2.
- [63] L. Oliva, L. Izzo, P. Longo, *Makromol. Rapid Commun.* 17 (1996) 745.
- [64] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2465.
- [65] N. Ishihara, M. Kuramoto, M. Uoi, Japanese Patent 62187708.
- [66] N. Ishihara, M. Kuramoto, M. Uoi, Japanese Patent 62104818.
- [67] N. Ishihara, M. Kuramoto, M. Uoi, European Patent 0,210,615 A2.
- [68] N. Ishihara, M. Kuramoto, M. Uoi, European Patent 0,224,097 A1.

- [69] N. Ishihara, M. Kuramoto, M. Uoi, US Patent 4,680,353.
- [70] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356.
- [71] H. Sato, Y. Tanaka, NMR analysis, *J. Polym. Sci. Polym. Phys. Ed.* 21 (1983) 1667.
- [72] Y. Inoue, A. Nishioka, R. Chujo, *Makromol. Chem.* 156 (1972) 207.
- [73] K. Matsuzaki, T. Uryu, K. Osada, T. Kawamura, *Macromolecules* 5 (1972) 816.
- [74] F.A. Bovey, F.P. Hood, E.W. Anderson, L.C. Snyder, *J. Chem. Phys.* 42 (1965) 3900.
- [75] F. Heatley, F.A. Bovey, *Macromolecules* 1 (1968) 301.
- [76] M. Kobayashi, T. Nakaoki, M. Uoi, *Polym. Preprints Jpn.* 37 (1988) 1187.
- [77] M. Kobayashi, T. Nakaoki, N. Ishihara, *Macromolecules* 22 (1989) 4377.
- [78] M. Karplus, *J. Am. Chem. Soc.* 85 (1963) 2870.
- [79] G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, M. Peraldo, *Chim. Ind. (Milan)* 38 (1956) 124.
- [80] A. Zambelli, P. Locatelli, E. Rigamonti, *Macromolecules* 12 (1969) 136.
- [81] A. Zambelli, M.C. Sacchi, P. Locatelli, G. Zann, *Macromolecules* 15 (1982) 211.
- [82] M.C. Sacchi, I. Tritto, P. Locatelli, D.R. Ferro, *Makromol. Chem. Rapid Commun.* 5 (1984) 731.
- [83] T. Takegami, T. Suzuki, *Bull. Chem. Soc. Jpn.* 43 (1970) 1484.
- [84] P. Locatelli, M.C. Sacchi, E. Rigamonti, A. Zambelli, *Macromolecules* 17 (1984) 124.
- [85] A. Zambelli, C. Tosi, M.C. Sacchi, *Macromolecules* 5 (1972) 649.
- [86] C. Pellicchia, P. Longo, A. Grassi, P. Ammendola, A. Zambelli, *Makromol. Chem. Rapid Commun.* 8 (1987) 277.
- [87] P. Ammendola, A. Zambelli, *Macromolecules* 19 (1986) 307.
- [88] P. Aaltonen, J. Seppala, *Eur. Polym. J.* 30 (1994) 683.