Polymerization of olefins with titanium and zirconium complexes containing hydrotris(pyrazolyl)borate or hydrotris(3,5-dimethylpyrazolyl)borate

Hiroshi Nakazawa [a,*], Shigeru Ikai [b], Kouji Imaoka [b], Yoshiyuki Kai [b],
Takefumi Yano [b]

[a] *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739, Japan*
[b] *Polymer Research Laboratory, Ube Industries, Ltd., Ichihara, Chiba 290, Japan*

Abstract

Zirconium and titanium complexes containing hydrotris(pyrazolyl)borate (Tp) or hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) as a ligand have been examined as polymerization precatalysts for ethylene, propylene and styrene. Activation of the group 4 transition-metal complexes by methylaluminoxane exhibits a greater catalytic activity in ethylene polymerization for $TpMCl_3$ (M = Zr, Ti) than for the corresponding mono-cyclopentadienyl analogue, $CpMCl_3$. Dimethyl substitution on the pyrazolyl groups enhances the activity for the Zr complex (Tp^*ZrCl_3), but not for the Ti complex (Tp^*TiCl_3). Complete substitution of O^tBu or OPh groups for Cl ligands in Tp^*ZrCl_3 greatly decreases the activity. Mono substitution of an OPh group for one Cl ligand in Tp^*TiCl_3 does not affect the activity. The addition of propylene comonomer reduces the catalytic activity of Zr complexes containing Tp or Tp^* to a considerable degree. The Tp and Tp^* complexes of Zr and Ti produce atactic polymers from styrene. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotris(pyrazolyl)borate; Titanium; Zirconium; Olefin; Polymerization

1. Introduction

In recent years, great progress in studies on homogeneous catalysts has been achieved for olefin polymerization. Most studies have been focused on metallocenes of group 4 transition metals described as Cp_2MX_2 (Cp = η^5-C_5H_5) and their derivatives as precatalysts, which are used with a cocatalyst such as methylaluminoxane (MAO). An active species derived from such a metallocene has been recognized to be a cationic 14-electron complex, $[Cp_2MR]^+$ (R = alkyl). In addition to metallocenes, half-metallocenes ($CpMX_3$) have been attracting increased attention. However, an active species derived from the half-metallocene, in particular half-titanocene, is not clearly identified. A cationic 10-electron species, $[CpMR_2]^+$ or more probably a base-coordinating cationic complex,

---

$[CpMR_2L]^+$ (L = solvent such as benzene or toluene) has been considered [1,2]. These active species seem to have lower stability in the catalytic system, which may be the main reason for the lower catalytic activity in olefin polymerization, though in cases of styrene [3,4] and conjugated diene [5,6] polymerization, a half-metallocene serves as an excellent precatalyst.

More recently, group 4 transition metal complexes containing no cyclopentadienyl ligand have also been developed as homogeneous polymerization catalysts. Among them are the complexes with a ligand such as amidinate [7,8], amido [9,10], oxazolin [11], porphyrin [12], alkoxy [13], aryloxy [14–16] and ketonate [17,18]. However, those complexes were found to have lower catalytic activity in ethylene and propylene polymerization relative to metallocenes.

In accordance with the research interest, we have paid attention to group 4 transition metal complexes with a hydrotris(pyrazolyl)borate (Tp) or hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) ligand, because they are considered as formal analogues of cyclopentadienide in terms of a uninegative 6-electron-donating ligand, but they are more electron-donative and bulkier than a Cp ligand. Until now, many transition metal complexes with poly(pyrazolyl)borate as a ligand have been investigated [19], but surprisingly little information has been reported on group 4 transition metal complexes containing poly(pyrazolyl)borate as polymerization catalysts for olefins [20,21] and styrene [22].

2. Experimental

2.1. Preparation of Zr and Ti complexes

The following complexes have been prepared according to literature methods: $TpZrCl_3$ [23], Tp^*ZrCl_3 [24], $Tp^*Zr(O^tBu)_3$ [23], $CpTpZrCl_2$ [25], $CpZrCl_3$ [26], $TpTiCl_3$ [27], Tp^*TiCl_3 [27] and $CpTiCl_3$ [28]. Cp_2ZrCl_2 was purchased from Wako Pure Chemical Ind. $Tp^*Zr(OC_6H_4Me-4)_3$ was synthesized (yield 70%) in a manner similar to that for $Tp^*Zr(OPh)_3$ [29]. $Tp^*TiCl_2(OC_6H_4X-4)$ (X = H, Me, CN) were newly prepared and the details will be reported elsewhere.
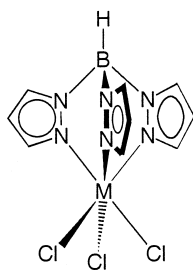
2.2. Polymerization

Modified methylaluminoxane (MMAO), which has isobutyl groups partly substituted for methyl groups in methylaluminoxane (MAO), was mainly used as a cocatalyst because MMAO has generally greater stability and greater solubility in a hydrocarbon solution than MAO. A toluene solution of MMAO, tri-isobutylaluminium (TIBA), trimethylaluminium (TMA) and trityl tetrakis(pentafluoro-phenyl)borate ($Ph_3CB(C_6F_5)_4$) were purchased from Tosoh-Akzo Corp. An organoaluminium compound (MMAO, TIBA and/or TMA) was charged in a reactor containing toluene and the reactor was saturated with a monomer gas. A toluene solution containing an adequate amount of a transition metal precatalyst was then added to the solution to give a total of 200 ml of toluene solution. The reaction mixture was stirred at an indicated temperature with the passage of the monomer gas (1000 ml/min) under atmospheric pressure. After 60 min, polymerization was terminated by adding ethanol with HCl.

The microstructure of polystyrene was determined by ^{1}H NMR analysis. Molecular weights (Mw and Mn) of olefin polymers were obtained by GPC analysis using *o*-dichlorobenzene as a solvent and polystyrene as a standard.
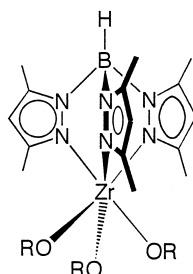
3. Results and discussion

In chart 1 are illustrated Zr and Ti complexes of which the polymerization activities were examined in this paper.

TpMCl$_3$ (M = Zr, Ti)
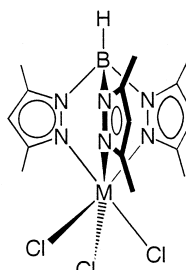
Tp*MCl$_3$ (M = Zr, Ti)

Tp*Zr(OR)$_3$ (R = CMe$_3$, C$_6$H$_4$Me-4)
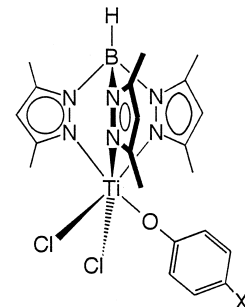
Tp*TiCl$_2$(OC$_6$H$_4$X-4) (X = H, Me, CN)
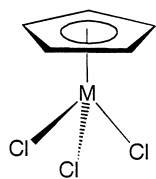
CpMCl$_3$ (M = Zr, Ti)
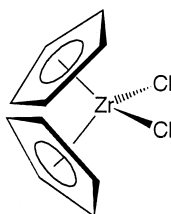
Cp$_2$ZrCl$_2$

TpCpZrCl$_2$

3.1. Olefin polymerization with Zr complexes containing Tp or Tp* as a ligand

Table 1 shows the results of ethylene and propylene (co)polymerization using TpZrCl$_3$ and TpCpZrCl$_2$ in combination with MMAO. The results for CpZrCl$_3$ and Cp$_2$ZrCl$_2$ are also listed in Table 1 for comparison.

Table 1
The results of olefin polymerization with zirconium complexes containing Tp or Tp[*]

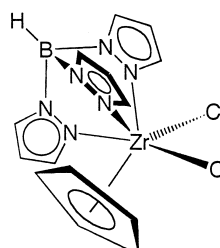| Run No.	Catalysts			Cocatalyst		Monomer E, P	Temp. (°C)	Activity (g P/mmol M)	Propylene contents (mol %)	Mw (10^4)	Mw/Mn
	complex	μmol	MMAO mmol	Al/metal mole ratio							
1	TpZrCl$_3$	10	0.5	50		E	40	79		37.6	15.0
2	TpZrCl$_3$	10	1	100		E	40	158		28.4	18.0
3	TpZrCl$_3$	10	10	1000		E	40	91		16.3	23.0
4	TpZrCl$_3$	10	1	100		E	60	83		5.41	9.1
5	TpZrCl$_3$	10	1	100		E	70	48		1.97	4.2
6	TpZrCl$_3$	10	1	100		E	80	20		1.28	3.3
7	TpZrCl$_3$	10	0.5	50		E/P (1/3)	40	24		1.60	4.7
8	TpZrCl$_3$	10	1	100		E/P (1/3)	40	63	8.2	0.67	2.4
9	TpZrCl$_3$	10	5	500		E/P (1/3)	40	14		1.44	4.5
10	CpZrCl$_3$	10	1	100		E	40	45			
11	CpZrCl$_3$	10	10	1000		E	40	26			
12	TpCpZrCl$_2$	10	1	100		E	40	750		28.0	5.1
13	TpCpZrCl$_2$	1	1	1000		E	40	808		14.9	3.9
14	TpCpZrCl$_2$	10	1	100		E/P (1/3)	40	99	5.9	3.83	3.9
15	TpCpZrCl$_2$	10	1	100		P	40	0			
16	Cp$_2$ZrCl$_2$	1	1	1000		E	40	10500		117	2.7
17	Cp$_2$ZrCl$_2$	0.4	4	10000		E	40	23600		75.8	2.6
18	Cp$_2$ZrCl$_2$	0.4	4	10000		E/P (3/1)	40	25200	9.6	8.30	2.2
19	Cp$_2$ZrCl$_2$	0.4	4	10000		P	40	450 (atactic)			

Polymerization conditions: Polym. time = 60 min; TpZrCl$_3$ was used as a CH$_2$Cl$_2$ slurry and TpCpZrCl$_2$ as a CH$_2$Cl$_2$ solution.

TpZrCl$_3$ is insoluble in toluene, whereas it is slightly soluble in CH$_2$Cl$_2$. Therefore, a CH$_2$Cl$_2$ solution (10 ml) containing TpZrCl$_3$, which looks like a slurry, was directly introduced into a toluene solution containing MMAO to start polymerization. Runs 1–9 show that TpZrCl$_3$ has a polymerization activity toward ethylene to some extent. Runs 1–3 and runs 7–9 were performed in order to obtain the most effective molar ratio of a cocatalyst and a catalyst (Al/metal) for ethylene polymerization and E/P copolymerization, respectively. The results showed that the best activity was obtained when the ratio is 100 in both cases, which contrasts with the fact that Cp$_2$ZrCl$_2$ requires ca. 10000 of the Al/metal ratio to show an optimal condition (see runs 16 and 17). Next, the Al/metal ratio was fixed at 100 and temperature dependence was examined (runs 2 and 4–6). Both the activity and the molecular weight of polyethylene decrease with an increase in polymerization temperature (40–80°C). The decrease in activity is more than that presumed from the lower solubility of ethylene monomer in toluene at a higher temperature: 31 mM at 40°C and 17 mM at 80°C were obtained by GC measurements. These results imply the gradual decomposition of an active species produced from TpZrCl$_3$ and MMAO under the polymerization conditions. The values of Mw/Mn are relatively large, indicating formation of more than one active species and/or the changing nature of the active species during the course of polymerization even at 40°C. It is hard, at present, to specify the real active species in the catalytic system. However, it is likely that the active species would be [TpZrMe$_2$]$^+$ because [Cp[*]TiMe$_2$]$^+$ has been proposed as an active polymerization catalyst [1,2] and that the deactivation of [TpZrMe$_2$]$^+$ would take place by the reduction of the central metal such as reductive elimination of the two alkyl groups.

Table 2
The results of olefin polymerization with Tp^*ZrCl_3

Run No.	Catalysts complex	Cocatalyst			Other cocat.			Monomer E, P	Activity (g P/mmol M)	Propylene content (mol %)	Mw (10^4)	Mw/Mn
		aluminium	mmol	Al/metal mole ratio	comp.	μmol	mole ratio					
20	Tp^*ZrCl_3	MMAO	1	100				E	730		151	4.6
21	Tp^*ZrCl_3	MMAO	1	100				E/P (19/1)	570	0.6	133	12.1
22	Tp^*ZrCl_3	MMAO	1	100				E/P (1/3)	279	15.8	35.6	6.5
23	Tp^*ZrCl_3	MMAO	5	500				E/P(1/3)	73			
24	Tp^*ZrCl_3	MMAO	20	2000				E/P(1/3)	21			
25	Tp^*ZrCl_3	MMAO	1	100				P	3		0.18	1.3
26	Tp^*ZrCl_3	TIBA	1	100	*1	10	1	E/P (1/3)	0			
27	Tp^*ZrCl_3	TMA	1	100	*1	10	1	E/P (1/3)	4	7.2	32.0	32.0
28	Tp^*ZrCl_3	MMAO	1	100	*1	10	1	E/P (1/3)	269	21.1	16.5	4.2

Polymerization conditions: amount of catalyst = 10 μmol; polym. temp. = 40°C; polym. time = 60 min; $*1 = Ph_3CB(C_6F_5)_4$.

The catalytic activity of $TpZrCl_3$ is not as excellent as that of Cp_2ZrCl_2 (runs 16 and 17)[1]. However, it should be noted that the activity is better than that of $CpZrCl_3$ (runs 10 and 11). This result indicates that a Tp ligand is preferable to a Cp ligand for an active species. It has been reported for Mo complexes that Tp is a better donor, especially a better π-donor toward a $[Mo(CO)_3]^+$ fragment than Cp [30]. If it is also applicable to our cases, a Tp ligand would donate more electron density to Zr than a Cp ligand, causing retardation of reductive deterioration of a catalytically active species.

A Zr complex $TpCpZrCl_2$ having both Tp and Cp ligands exhibited a higher level of polymerization activity for ethylene (runs 12 and 13), but the activity is far less than that of Cp_2ZrCl_2 (runs 16 and 17). This shows that the replacement of Cp by Tp in Cp_2ZrCl_2 is not preferable, in this case, in terms of polymerization activity. This can be accounted for by a prevailing steric effect of a Tp ligand. A Tp is reported to be a bulky ligand: the maximum cone angle of a Tp ligand has been calculated to be ca. 180° [30]. On going from homopolymerization of ethylene to E/P copolymerization, the reduction of activity was observed for both $TpZrCl_3$ (run 2 versus 8) and $TpCpZrCl_2$ (run 12 versus 14), whereas comonomer enhancement was observed for Cp_2ZrCl_2 (run 17 versus 18). The degree of deterioration is larger for $TpCpZrCl_2$ than for $TpZrCl_3$. This is also reasonably explained in terms of the bulkiness of a Tp ligand: $TpCpZrCl_2$ is more crowded around a Zr atom. The influence of a bulky Tp ligand on polymerization was also observed in propylene polymerization: no propylene polymerization occurred with $CpTpZrCl_2$/MMAO (run 15), whereas the catalyst system, Cp_2ZrCl_2/MMAO had some activity (run 19).

Table 2 lists the results of ethylene and propylene homo and copolymerization with Tp^*ZrCl_3 corresponding to methyl-substituted $TpZrCl_3$. The comparison of the data of run 2 with those of run 20 shows that the dimethyl substitution increases the activity of ethylene polymerization about five times and increases the value of Mw. The greater activity can be attributed to the greater electron-donating ability of Tp^* which resists the reductive decomposition of an active species.

Polymerization activity and Mw decreased with a propylene comonomer (runs 21 and 22) as observed for $TpZrCl_3$. In the case of propylene homopolymerization (run 25), a great decrease in the activity was observed as for $TpCpZrCl_2$ and Cp_2ZrCl_2.

[1] In the case of Cp_2ZrCl_2, its catalytic activity is extremely great compared with those for $TpZrCl_3$, $CpZrCl_3$ and $TpCpZrCl_2$. In order to keep a solution temperature constant (40°C), 1 μmol and 0.4 μmol (not 10 μmol) of the catalyst (Cp_2ZrCl_2) were employed.

For E/P copolymerization, the influence of the Al/metal ratio on the catalytic activity was examined (runs 22–24). When the ratio is 100, the activity is greatest and it decreases with an increase in the ratio.

Next, in order to examine whether MMAO is indispensable or not in the E/P copolymerization by using Tp^*ZrCl_3, runs 26 and 27 were carried out where $Ph_3CB(C_6F_5)_4$ and either TIBA or TMA were used as cocatalysts. No activities and almost no activities were observed. The reason may arise from deactivation of an active species (presumably $[Tp^*ZrR_2]^+$) by interaction with $[B(C_6F_5)_4]^-$ or $[RB(C_6F_5)_3]^-$ as is observed in a half-metallocene system [1,2,31]. An interesting point is that the combination of $Ph_3CB(C_6F_5)_4$ with MMAO did not deactivate the polymerization (run 28 versus 22). Therefore, it can be said that MMAO plays, in addition to a role of alkylation of Tp^*ZrCl_3, an important role in some ways such as prevention of interaction with a borate mentioned above. The details are, however, unclear now.

Table 3 shows the productivities of ethylene and propylene homo and copolymerization catalyzed by $Tp^*Zr(OR)_3$, three chlorine atoms of Tp^*ZrCl_3 being replaced by t-butyloxy (O^tBu) or p-methylphenoxy (OC_6H_4Me-4) groups. We expected that the t-butyloxy and phenoxy groups in $Tp^*Zr(O^tBu)_3$ and $Tp^*Zr(OC_6H_4Me$-4$)_3$ were alkylated by MMAO to give $[Tp^*ZrMe_2]^+$ or $[Tp^*ZrMe(OR)]^+$. However, the results showed no substantial activity (runs 29–33). The results imply that the Zr–OR bond is inert toward the alkylating reagent, which is consistent with the previous reports in which a double bond character in a Zr–OR bond is demonstrated by the X-ray structures of Zr complexes with Tp^* and OR ligands [29,32].

Another possible explanation for the results of runs 29–33 is that the substitution of OR in $Tp^*Zr(OR)_3$ by MMAO takes place but the active species is considerably deactivated by the interaction with an Al–OR moiety newly formed. However, the results of run 34 rule out the possibility. $Me_2Al(OPh)$ was used as a model compound containing an Al–OR moiety being expected to be formed in the reaction of $Tp^*Zr(OR)_3$ with MMAO. The addition of $Me_2Al(OPh)$ in the amount of up to ten equivalents relative to Tp^*ZrCl_3 did not cause any substantial decrease in activity (run 34), though the addition of 50 times the amount of $Me_2Al(OPh)$ caused deactivation (run 35). Therefore, $Me_2Al(OPh)$ does not seem to be a strong enough base to deactivate an active species by coordinating through its oxygen. On the other hand, the addition of PhOMe, being much more basic than $Me_2Al(OPh)$, to the Tp^*ZrCl_3/MMAO catalytic system resulted in strong deactivation

Table 3

The results of olefin polymerization with zirconium complexes containing Tp^*

Run No.	Catalysts complex	μmol	Cocatalyst aluminium	mmol	Al/metal mole ratio	Other cocat. comp.	μmol	mole ratio	Monomer E, P	Activity (g P/mmol M)	Mw (10^4)	Mw/Mn
29	$Tp^*Zr(O^tBu)_3$	10	MMAO	1	100				E	11	311.1	166.6
30	$Tp^*Zr(O^tBu)_3$	10	MMAO	1	100				E/P (1/3)	2		
31	$Tp^*Zr(O^tBu)_3$	10	MMAO	5	500				E/P (1/3)	2		
32	$Tp^*Zr(OC_6H_4Me$-4$)_3$	10	MMAO	1	100				E	2	188.1	53.2
33	$Tp^*Zr(OC_6H_4Me$-4$)_3$	5	MMAO	5	1000				E	8		
34	Tp^*ZrCl_3	10	MMAO	1	100	$AlMe_2OPh$	100	10	E/P (1/3)	297	19.9	2.8
35	Tp^*ZrCl_3	10	MMAO	1	100	$AlMe_2OPh$	500	50	E/P (1/3)	0		
36	Tp^*ZrCl_3	10	MMAO	1	100	MeOPh	10	1	E/P (1/3)	258	22.1	1.8
37	Tp^*ZrCl_3	10	MMAO	1	100	MeOPh	30	3	E/P (1/3)	138	21.2	2.6
38	Tp^*ZrCl_3	10	MMAO	1	100	MeOPh	100	10	E/P (1/3)	44	23.9	3.9

Polymerization conditions: polym. temp. = 40°C; polym. time = 60 min.

(runs 36–38). MMAO does not seem to be a strong enough Lewis acid to hold PhOMe for preventing the coordination of the ether to a zirconium active center.

3.2. Olefin polymerization with Ti complexes containing Tp or Tp* as a ligand

The results of ethylene polymerization with $TpTiCl_3$ are listed in Table 4. The solubility of $TpTiCl_3$ in toluene was very poor and so a homogeneous CH_2Cl_2 solution of $TpTiCl_3$ (10 ml) was added to toluene (190 ml) containing MMAO and saturated with ethylene to start a polymerization.

As is observed in the case of the zirconium complexes, both $TpTiCl_3$ and Tp^*TiCl_3 showed catalytic activity. In these cases, when the ratio of Al/Ti is 1000, the activity seems optimal (runs 39–41 and 45–46). The activity decreased with an increase in polymerization temperature (runs 40, 42, 43 and 46–48). $TpTiCl_3$ is more active than the Cp analogue (run 40 versus 44), indicating that a Tp ligand is preferable to a Cp ligand for ethylene polymerization as is observed for the corresponding Zr complexes. $TpTiCl_3$ is less active than the Zr analogue. This may be due to the lower stability of the Ti active species.

The comparison of activities of $TpTiCl_3$ and Tp^*TiCl_3 (run 40 versus 46, 42 versus 47 and 43 versus 48) shows that the dimethyl substitution on the pyrazolyl groups does not improve the activity, which is different from the Zr case. In a smaller Ti case, the steric effect of Tp^* on ethylene polymerization (decreasing the catalytic activity) may cancel the electronic effect (increasing the activity).

Runs 49–52 show the results of $Tp^*Ti(OR)Cl_2$ having one OR and two Cl ligands. There has been no dramatic decrease in activity, but rather a slight increase. The active species is assumed to be $[Tp^*Ti(OC_6H_4X\text{-}4)R]^+$, and the phenoxy group may stabilize it by π donation from O to Ti. The effect of X (H, Me, CN) on activity was not observed. Another interesting point here is that $TIBA/Ph_3CB(C_6F_5)_4$ is able to function as an effective cocatalyst (run 50). This result may imply that the coordination of the $[B(C_6F_5)_4]^-$ or $[RB(C_6F_5)_3]^-$ anion to an active species is prevented by the electron-donating effect and sterically crowded effect of both Tp^* and phenoxy ligands.

Table 4
The results of ethylene polymerization with titanium complexes containing Tp or Tp^*

Run No.	Catalysts complex	Cocatalyst			Other cocat.	Temp. (°C)	Activity (g P/mmol M)	Mw (10^4)	Mw/Mn
		aluminium	mmol	Al/metal mole ratio					
39	$TpTiCl_3$ *1	MMAO	1	200		40	28		
40	$TpTiCl_3$ *1	MMAO	5	1000		40	41	103	74.2
41	$TpTiCl_3$ *1	MMAO	25	5000		40	35	20.5	62.2
42	$TpTiCl_3$ *1	MMAO	5	1000		60	19	103	66.2
43	$TpTiCl_3$ *1	MMAO	5	1000		80	3	49.5	11.6
44	$CpTiCl_3$	MMAO	5	1000		40	13		
45	Tp^*TiCl_3	MMAO	1	200		40	10		
46	Tp^*TiCl_3	MMAO	5	1000		40	50		
47	Tp^*TiCl_3	MMAO	5	1000		60	19	129	42.2
48	Tp^*TiCl_3	MMAO	5	1000		80	6	72.8	23.2
49	$Tp^*Ti(OPh)Cl_2$	MMAO	5	1000		40	54		
50	$Tp^*Ti(OPh)Cl_2$	TIBA	2.3	43	*2	40	74		
51	$Tp^*Ti(OC_6H_4Me\text{-}4)Cl_2$	MMAO	5	1000		40	60		
52	$Tp^*Ti(OC_6H_4CN\text{-}4)Cl_2$	MMAO	5	1000		40	52		

Polymerization conditions: amount of catalyst = 5 μmol; polym. time = 60 min; *1 = used as a CH_2Cl_2 solution; *2 = $Ph_3CB(C_6F_5)_4$(5 μmol).

Table 5
The results of styrene polymerization with Ti and Zr complexes containing Tp or Tp*

Run No.	Catalysts		Cocatalyst		Styrene (ml)	Temp (°C)	Activity (g P/mmol M h)	Mw (10^4)	Mw/Mn	Microstructure (%)
	complex	μmol	MMAO mmol	Al/metal mole ratio						
53	CpTiCl$_3$	5	5	1000	11.5	40	325	3.59	2.1	syndiotactic
54	TpTiCl$_3$ *1	10	10	1000	23	40	580	oily		atactic
55	Tp*TiCl$_3$	10	10	1000	23	40	11			atactic
56	TpZrCl$_3$	10	1	1000	11.5	40	6			atactic
57	TpZrCl$_3$	10	1	1000	11.5	60	83	5.41	9.1	atactic
58	TpZrCl$_3$	10	1	1000	11.5	70	48	1.97	4.2	atactic
59	Tp*ZrCl$_3$	10	1	1000	11.5	40	10	1.37	3.8	atactic

Polymerization conditions: polym. time = 60 min; *1 = used as a CH$_2$Cl$_2$ solution.

3.3. Styrene polymerization with Zr and Ti complexes containing Tp or Tp*

The combination of half-titanocenes such as CpTiCl$_3$ and Cp*TiCl$_3$ with MAO is known to yield active catalysts for syndiospecific polymerization of styrene. Active species from the half-titanocenes have been assumed to be cationic cyclopentadienyl Ti(III) complexes [4,33,34].

With this background, it is interesting to investigate styrene polymerization with TpMCl$_3$ and Tp*MCl$_3$ (M = Zr, Ti) being isoelectronic to half-metallocenes. The results, together with those for the Cp analogue, are shown in Table 5.

Although CpTiCl$_3$ produced syndiotactic polystyrene in a high yield (run 53), both TpTiCl$_3$ and Tp*TiCl$_3$ gave only atactic polystyrene (runs 54 and 55). The activity of TpTiCl$_3$ is relatively high. From the high activity and atactic polystyrene formation, we propose that this polymerization proceeds not by a coordination mechanism but by a cationic mechanism. For example, a proposed [TpTiMe$_2$]$^+$ species abstracts a Cl$^-$ anion from the solvent CH$_2$Cl$_2$ to give [CH$_2$Cl]$^+$ which initiates cation polymerization of styrene. In the Tp*TiCl$_3$/MMAO system, a cationic polymerization mechanism does not seem operative due to weakened Lewis acidity of the active species [Tp*TiMe$_2$]$^+$ by coordinating an electron-donating Tp* ligand. The lower activity and the formation of a non-stereoregular polymer may arise from the great steric hindrance of a Tp* ligand which interferes with both the interaction of the phenyl ring of the styrene monomer and the subsequent 2,1-insertion of the monomer into a metal alkyl bond.

TpZrCl$_3$ and Tp*ZrCl$_3$ produced only a low amount of atactic polymers (runs 56 and 59). The results on activity and polymer structure are identical with the results reported for half-zirconocenes [3]. This tendency and the relationship between the temperature and the activity of styrene polymerization (runs 56–58) suggest that the polymerization takes place not by a cationic mechanism but by a coordination mechanism.

4. Conclusions

It was found that TpMCl$_3$ (M = Ti, Zr) serves as a catalyst in combination with MMAO for olefin polymerization. The catalytic activity is higher than that of the Cp analogue CpMCl$_3$. The substitution of Tp* for Tp in TpZrCl$_3$ causes greater activity. These results are reasonably explained by a better electron-donating ability for Tp than for Cp, and for Tp* than for Tp. TpCpZrCl$_2$ shows lower catalytic activity than Cp$_2$ZrCl$_2$. Tp is bulkier than Cp, which may cause the low activity of

TpCpZrCl$_2$. Tp*TiCl$_3$ exhibits activity similar to that of TpTiCl$_3$, which is in contrast to the corresponding Zr case. The electronic effect is canceled by the steric effect for the relatively small Ti complex. Introduction of Tp or Tp* seems to make a catalytic species more active by its electron-donating ability and to make the species less active by its steric bulkiness. The activity is due to a critical balance of the two opposite effects.

References

[1] J.D. Gillis, M. Tudoret, M.C. Baird, J. Am. Chem. Soc. 115 (1993) 2543.
[2] R. Quyoum, Q. Wang, M. Tudoret, M.C. Baird, J. Am. Chem. Soc. 116 (1994) 6435.
[3] N. Ishihara, M. Kuramoto, M. Uoi, Macromolecules 21 (1988) 3356.
[4] P. Longo, A. Proto, L. Oliva, Macromol. Rapid Commun. 15 (1994) 15.
[5] G. Ricci, L. Porri, A. Giarrusso, Macromol. Symp. 89 (1995) 383.
[6] P. Longo, P. Oliva, A. Proto, A. Zambelli, Gazz. Chim. Ital. 126 (1996) 377.
[7] D.H. Korine, M.S. Eisen, J. Organomet. Chem. 503 (1995) 307.
[8] J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 14 (1995) 2106.
[9] A.D. Horton, J. de With, A.J. van der Linden, H. van de Weg, Organometallics 15 (1996) 2672.
[10] J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vittal, Macromolecules 29 (1996) 5241.
[11] P.G. Cozzi, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 14 (1995) 4994.
[12] H. Brand, J.A. Capriotti, J. Arnold, Organometallics 13 (1994) 4469.
[13] M. Mitani, K. Oouchi, M. Hayakawa, T. Yamada, T. Mukaiyama, Polymer Bull. 34 (1995) 199.
[14] G. Conti, G. Arribas, A. Altomare, F. Ciardelli, J. Mol. Catal. 89 (1994) 41.
[15] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.
[16] T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Makromol. Chem. Rapid Commun. 10 (1989) 349.
[17] K. Oouchi, M. Mitani, M. Hayakawa, T. Yamada, T. Mukaiyama, Makromol. Chem. Phys. 197 (1996) 1545.
[18] C. Janiak, T.G. Scharmann, K.C.H. Lange, Macromol. Rapid Commun. 15 (1994) 655.
[19] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[20] Asahi Chemicals, Japanese Laid Patent, 70224, 1995.
[21] Tonen Chemicals, Japanese Laid Patent, 95110, 1989.
[22] Dow Chemicals, Japanese Laid Patent, 305585, 1992.
[23] D.L. Reger, M.E. Tarquini, Inorg. Chem. 22 (1983) 1064.
[24] D.L. Reger, M.E. Tarquini, Inorg. Chem. 21 (1982) 840.
[25] D.L. Reger, R. Mahtab, J.C. Baxter, L. Lebioda, Inorg. Chem. 25 (1986) 2046.
[26] G. Erker, K. Berg, L. Treschanke, K. Engel, Inorg. Chem. 21 (1982) 1277.
[27] J.K. Kouba, S.S. Wreford, Inorg. Chem. 9 (1976) 2313.
[28] A.M. Cardoso, R.J.H. Clark, S. Moorhouse, J. Chem. Soc. Dalton 7 (1980) 1156.
[29] R.A. Kresinski, L. Isam, T.A. Hamor, C.J. Lones, J.A. McCleverty, J. Chem. Soc. Dalton Trans. (1991) 1835.
[30] M.D. Curtis, K. Shiu, W.M. Butler, J.C. Huffman, J. Am. Chem. Soc. 108 (1986) 3335.
[31] R. Gomez, M.H. Green, J. Haggitt, J. Chem. Soc. Dalton Trans. (1996) 939.
[32] D.L. Reger, M.E. Tarquini, L. Lebioda, Organometallics 2 (1983) 1763.
[33] A. Grassi, A. Zambelli, Organometallics 15 (1996) 480.
[34] D.J. Duncalf, H.J. Wade, C. Waterson, P.J. Derrick, D.M. Haddleton, A. McCamley, Macromolecules 29 (1996) 6399.