Butadiene polymerization with various half-titanocenes

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Abstract

The polymerizations of butadiene were performed with various half-titanocenes in combination with either modified methylalumoxane (MMAO) or $(C_6H_5)_3CB(C_6F_5)_4$/trialkylaluminum and the latter activator showed higher catalyst activities. The substitution of an alkyloxy group for a Cl atom in $CpTiCl_3$ decreased activity and did not change the microstructure of polymers. $CpTiBr_3$ and half-titanocenes with substituents on a Cp ring exhibited lower activities, but the microstructure of higher vinyl unit contents. The results of activity suggest cationic active species of $Ti(+4)$. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, metallocenes as single site catalysts for olefin polymerization have been of great advantage in that polymer microstructure can be controlled by designing the structure of the ligands.

Concerning conjugated diolefins, Zambelli et al. [1–3] and Ricci et al. [4–7] have extensively examined the metallocenes of titanium, zirconium, and vanadium activated by methylalumoxane (MAO) as catalysts. The catalyst activity and the selectivity of *trans*, vinyl, and *cis* units in polymers remarkably varied depending upon the structure of 1,3-diolefins polymerized and polymerization temperature. Among the

half-titanocenes with a different oxidation state of titanium, $CpTiCl_2$ is more active than $CpTiCl_3$ in combination with MAO indicating an active species with an oxidation state of three. In the comparison of catalyst activities between the di-Cp and the mono-Cp titanium complexes, the former showed appreciably lower activity, presumably because of an excessive outer sphere electron number; four and three electrons from a diolefin and an allylic polymer chain end moiety coordinated to titanium, respectively, in addition to 10 electrons of the two Cp ligands.

Recently, the enhancement of activity and syndio-specificity in styrene polymerization have been reported on the catalyst systems, $CpTiX_3$ and MAO where all three X's or a part of the X's as σ ligands are iodine [8] and

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alkyloxy groups [9,10]. With respect to 1,3-butadiene being an important monomer for the production of various elastomers, a study on the influence of the ligand structure of metallocenes is still very few on catalytic activity and polymer microstructures.

2. Experimental

2.1. Pre-catalyst complexes and co-catalysts

Half-titanocenes as pre-catalysts have been prepared by the methods reported; $CpTiCl_3$ and $CpTiBr_3$ [11], $Cp*TiCl_3$, $Cp*TiBr_3$ and $Cp*TiI_3$ [12], $(Ind)TiCl_3$ [13], $CpTiCl_2(OR)$ R = OMe [14], OEt, O-isoPr [15]. $Me_2SiCp*(N$-$tBu)TiCl_2$ was purchased from Kanto Chemical. We obtained co-catalysts from TOSOH AKZO, as toluene solutions of triisobutylaluminum (TIBA), triethylaluminum (TEA), modified methylalumoxane (MMAO) which comprises hydrolyzed triisobutylaluminum in part together with hydrolyzed trimethylaluminum, and a powder of $(C_6H_5)_3CB(C_6F_5)_4$. MMAO was used instead of MAO because of the stability and solubility in a hydrocarbon.

2.2. Polymerization procedure

Butadiene polymerizations were carried out for 60 min in a mixture of toluene and butadiene (168 ml/32 ml) in a 300 ml flask by adding the toluene solutions of pre-catalyst and co-catalyst. The complex of 5 μmol was used together with either MMAO of 5 mmol (Al/Ti = 1000) or $(C_6H_5)_3CB(C_6F_5)_4$ of 7.5 μmol (B/Ti = 1.5) and TIBA of 0.2 mmol(Al/Ti = 200) or TEA of 0.5 mmol (Al/Ti = 100). The pre-catalyst and the co-catalyst were introduced into a polymerization medium in the following order: (1) MMAO and a titanium complex, or (2) TIBA or TEA, $(C_6H_5)_3CB(C_6F_5)_4$, and a titanium complex. Polymerization was terminated by adding an antioxidant of Irganox 1076 dissolved in a HCl–MeOH solution.

2.3. Polymer analysis

Molecular weights (M_n and M_w) were obtained by gel permeation chromatography using polystyrene as a standard sample. Microstructures were determined by an IR spectrometer for CS_2 solutions of polymers measuring absorption peaks at 740 cm, 910 cm, and 980 cm for *cis*, vinyl, and *trans* units, respectively.

3. Results and discussion

Table 1 indicates the results of butadiene polymerization with various half-titanocenes having no substituents on the Cp ring in combination with modified methylalumoxane (MMAO), or $(C_6H_5)_3CB(C_6F_5)_4$ and triiso-

Table 1
The results of butadiene polymerization with various half-titanocenes

Run No.	Catalyst structure	Co-catalyst	Polym. T (°C)	Activity (gP/mmol Ti · h)	M_w (10^{-4})	M_w/M_n	Microstructure (%)		
							trans	vinyl	*cis*
1	$CpTiCl_3$	MMAO	30	509	221	1.82	1.1	15.2	83.6
2	$CpTiBr_3$	MMAO	30	210	281	2.21	1.00	21.3	77.7
3	$CpTiCl_2(OMe)$	MMAO	30	157	228	1.98	1.1	15.1	83.8
4	$CpTiCl_2(OEt)$	MMAO	30	176	241	1.72	1.2	15.00	83.8
5	$CpTiCl_2(O\text{-}iso Pr)$	MMAO	30	162	225	1.98	1.6	15.1	83.3
6	$CpTiCl_3$	Borate/TEA	30	1240	209	1.88	1.00	15.1	83.9
7	$CpTiBr_3$	Borate/TIBA	30	420	246	2.53	0.90	20.70	78.4
8	$CpTiCl_2(OMe)$	Borate/TEA	30	1010	223	2.03	1.2	15.2	83.6
9	$CpTiCl_2(OEt)$	Borate/TEA	30	798	194	1.84	1.1	14.9	84.00
10	$CpTiCl_2(O\text{-}iso Pr)$	Borate/TEA	30	365	190	2.05	1.00	15.00	84.00

butylaluminum (TIBA) or triethylaluminum (TEA).

Butadiene polymerization with CpTiCl$_3$ and MMAO has been performed in an Al/Ti ratio of 1000 which was the reported polymerization condition in the literatures [3–7]. CpTiCl$_3$ activated by MMAO has a relatively high activity (Run 1) and the molecular weight (M_w) of the polymer is quite high (over 2 million) and the molecular weight distribution is around 2.0 indicating a single site catalyst system and a homogeneous polymerization system. The contents of *trans*, vinyl, and *cis* units are about 1, 15, and 84%, respectively. Until now, we have seen no single report on the catalyst properties of CpTiCl$_3$ with a borate ionic compound and an alkylaluminum in butadiene polymerization. The combination of CpTiCl$_3$ with TEA does not show substantial activity of butadiene polymerization. However, the use of $(C_6H_5)_3CB(C_6F_5)_4$ with CpTiCl$_3$ and TEA gave a highly active catalyst system (Run 6). This supports the formation of a cationic titanium complex as active species. A type of co-catalyst used in the present study did not influence on microstructure but activity.

The substitution of Br atoms for Cl atoms in CpTiCl$_3$ decreased activity by about 60% for both MMAO and $(C_6H_5)_3CB(C_6F_5)_4$/TIBA activators (Run 2 and 7). The other remarkable differences are a 6% increase in a vinyl content and a decrease of the same percent in a *cis* content.

The data from Run 3 to 5 and Run 8 to 10 show the influence of the substitution of an alkyloxy group for one of the Cl atoms in CpTiCl$_3$ on catalyst properties. Dramatic changes are seen in activity while the polymer structures remain unchanged. For the MMAO activator, the activities decreased in a great extent for three different alkyloxy groups. On the other hand, with the use of the borate compound the activities decreased with an increase in the size of the alkyloxy groups.

Until now, Ricci et al. [4] proposed a cationic titanium(+3) active species (Fig. 1) for the
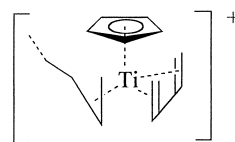

Fig. 1.

CpTiCl$_3$/MAO catalyst system for conjugated diolefin polymerization just as frequently stated in the case of styrene polymerization. If so, the structure of active species derived from the half-titanocenes, CpTiCl$_3$, CpTiBr$_3$ and CpTiCl$_2$(OR) should be the same.

With respect to the observed difference in activity among the half-titanocenes, one may propose the following reasons: the alkylation of CpTiBr$_3$ or CpTiCl$_2$(OR) by an organoaluminum compound followed by the reduction from Ti(+4) to Ti(+3) (Eq. (1)) or the abstraction of Br or OR anion by MMAO or $(C_6H_5)_3CB(C_6F_5)_4$ to give rise to the Ti(+3) active species (Eq. (2)) is a slower step compared to the case of CpTiCl$_3$.

$$CpTiCl_2(OR) \rightarrow CpTiR_2(OR) \rightarrow CpTiR(OR) \qquad (1)$$

$$CpTiR(OR) \rightarrow [CpTiR]^+ \qquad (2)$$
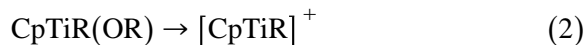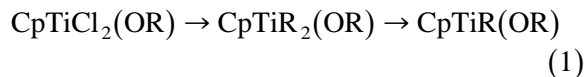
In order to find out some answers to the above proposal, the polymerization profiles were obtained for the both catalyst systems, CpTiCl$_3$ and CpTiCl$_2$(*O-iso*Pr) with the $(C_6H_5)_3CB(C_6F_5)_4$/TEA co-catalyst (Fig. 2). For the former catalyst system, the conversion increased rapidly with a polymerization time but gradually after a polymerization time of about 60 min mainly because of a reduced butadiene concentration. On the other hand, the latter catalyst system shows a linear increase in conversion with time without an increase of activity, indicating an invariable number of active species during a course of polymerization. Also, you see similarly small M_w/M_n values (ca. 2.0) for the polymers shown in the Fig. 2.

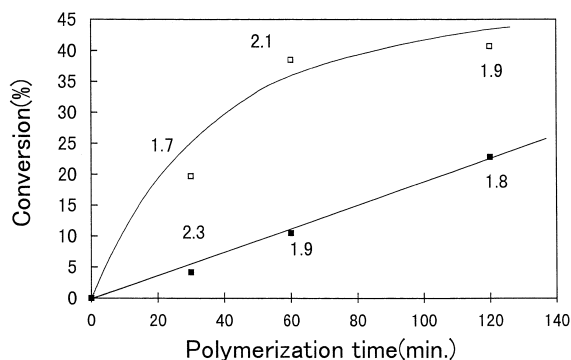Further more, CpTiCl$_2$(OEt) was treated with MMAO at 28°C for 120 min before the intro-

Fig. 2. Polymerization profiles for CpTiCl$_3$ (□) and CpTiCl$_2$(O-isoPr) (■), with numbers in the figure indicating M_w / M_n values for each polymer produced.

duction of butadiene. The activity (260 g/mmol Ti · h) was found to be nearly a half of that for the CpTiCl$_3$/MMAO catalyst system. From these results, it can be said that the observed lower activity for the CpTiCl$_2$(OR) pre-catalyst is neither due to the slow formation of the active species nor the rapid destruction of it in a polymerization time of 120 min.

Then, it is considered that the active species derived from CpTiCl$_2$(OR) is different from that from CpTiCl$_3$. The alkylation of CpTiCl$_2$(OR) to give CpTiR$_2$(OR) and the subsequently occurring abstraction of the alkyl anion might give the cationic Ti(+4) active species [CpTiR(OR)]$^+$. As matter of fact, cationic Ti(+4) half-titanocenes, [Cp*TiMe$_2$]$^+$ and [Cp*TiMe$_2$(arene)]$^+$ are well studied by Baird et al. for olefin and styrene polymerizations [16–18]. The ligand X (alkyl, halogen, alkyloxy) in CpTiX$_3$ should determine the activity, as well as the polymer microstructures. It can-

not be explained now why the alkyloxy ligands interfere with the polymerization activity in a different way between MMAO and (C$_6$H$_5$)$_3$-CB(C$_6$F$_5$)$_4$/TEA.

The effects of the substituents on the Cp ring of CpTiX$_3$ were also examined for different halogen atoms (Table 2). A half-titanocene bearing an indenyl ligand instead of a Cp ligand shows lower activity and microstructure with 6 and 3% higher vinyl and *trans* contents, respectively (Run 11). The half-titanocenes having a pentamethyl Cp ligand (Cp*) are far less active suggesting intensive steric hindrance presumably by the five methyl groups on the Cp ring (Run 12, 13, 14). The polymer structures are, however, the same regardless of halogen ligands of Cp*TiX$_3$ as that for (Ind)TiCl$_3$. Run 15 shows the result for a so-called constrained geometry catalyst (CGC). The values of activity and microstructure indicate that a steric environment around a central Ti in the CGC is similar to that for the half-titanocenes Cp*TiX$_3$. The CGC with a MAO co-catalyst commercially used at present for olefin polymerization is well-known to be one of highly active catalyst systems, being quite different from the Cp*TiCl$_3$/MAO catalyst system. A σ bond between a Ti atom and a *N*(*t*-Bu) group of the complex is believed to be inert toward alkylation by an alkylaluminum compound. In fact, a cationic Ti(+4) complex, [Me$_2$SiCp*(*N*-*t*Bu)TiMe]$^+$ was recently reported as an active species for olefin polymerization [19,20]. This is also one of our bases to assume the cationic Ti(+4) active species for butadiene polymerization.

Table 2
The results of butadiene polymerization with substituted half-titanocenes

Run no.	Catalyst structure	Co-catalyst	Polym. T (°C)	Activity (gP/mmol · h)	Microstructure (%)		
					trans	vinyl	*cis*
11	(Ind)TiCl$_3$	MMAO	30	181	4.6	20.3	75.1
12	Cp*TiCl$_3$	MMAO	40	40	3.5	21.0	75.5
13	Cp*TiBr$_3$	MMAO	40	46	3.7	20.8	75.5
14	Cp*TiI$_3$	MMAO	40	11	5.1	21.0	73.9
15	Me$_2$SiCp*(*N*-*t*Bu)TiCl$_2$	MMAO	40	33	3.5	23.1	73.4

Concerning the polymer microstructures, they were found to vary in a rather limited range (Tables 1 and 2); 1 to 5% for *trans* units, 15 to 23% for vinyl units, and 84 to 74% for *cis* units. First, these changes can be attributed to a steric effect of the Cp ligand with the substituents on its ring, as well as the σ ligand X. However, as seen before, $CpTiCl_2(OR)$ gave the polymers with about the same polymer structure (Run 3 to 5 and 8 to 10), though $CpTiBr_3$ (Run 2 and 7) did higher vinyl unit contents relative to $CpTiCl_3$ (Run 1 and 6). Hence, on a second thought, it can be necessary to consider an electronic effect rather than a steric one for the observed change of polymer structure; the variation of electron density of a titanium metal. At present, it is quite difficult to reveal a plausible explanation on the change of microstructure in particular for the $CpTiBr_3$ catalyst system.

References

[1] P. Longo, P. Oliva, A. Proto, A. Zambelli, Gazzetta Chimica Italiana 126 (1996) 377.

[2] A. Peluso, R. Improta, A. Zambelli, Macromolecules 30 (1997) 2219.

[3] P. Longo, A. Peluso, P. Oliva, A. Zambelli, Macromolecules 29 (1996) 5500.

[4] G. Ricci, S. Italia, A. Giarrusso, L. Porri, J. Organomet. Chem. 451 (1993) 67.

[5] G. Ricci, A. Giarrusso, L. Porri, Macromol. Symp. 89 (1995) 383.

[6] G. Ricci, C. Bosisio, L. Porri, Macromol. Rapid Commun. 17 (1996) 781.

[7] G. Ricci, A. Panagia, L. Porri, Polymer 37 (1996) 363.

[8] W. Kaminsky, 2nd International Congress on Metallocene Polymers Metallocenes '96, Dusseldorf, Germany, March, Schotland Business Research.

[9] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polymer Bull. 37 (1996) 719.

[10] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polymer J. 29 (1997) 182.

[11] A.M. Cardoso, R.J.H. Clark, S. Moorhouse, J. Chem. Soc., Dalton Trans. 7 (1980) 1156.

[12] G.H. Llinas, M. Mena, F. Palacios, P. Royo, R. Serrano, J. Organomet. Chem. 340 (1988) 37.

[13] T.E. Ready, R.O. Day, J.C.W. Chain, D. Rausch, Macromolecules 26 (1993) 5822.

[14] R.D. Gorsich, J. Am. Chem. Soc. 82 (1960) 4211.

[15] I.M.M. Fassing, D. Pletcher, R.C. Whitby, J. Organomet. Chem. 470 (1994) 109.

[16] D.J. Gillis, M.J. Tudoret, M.C. Baird, J. Am. Chem. Soc. 115 (1993) 2543.

[17] R. Quyoum, Q. Wang, M.J. Tudoret, M.C. Baird, J. Am. Chem. Soc. 116 (1994) 6435.

[18] Q. Wang, M.C. Baird, Macromolecules 28 (1995) 8021.

[19] Y. Chen, C.L. Stern, S. Yang, T. Marks, J. Am. Chem. Soc. 118 (1996) 12451.

[20] Y. Chen, C.L. Stern, T. Marks, J. Am. Chem. Soc. 119 (1997) 2582.