Kinetic Evaluation of Various Isospecific Active Sites on $MgCl_2$-Supported Ziegler Catalysts

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SUMMARY: The formation, variation and conversion of isospecific active sites were investigated, based on the isotacticity distribution of the polypropenes analyzed by the temperature rising elution fractionation (TREF) method. Stopped-flow polymerization of propene was carried out with a $MgCl_2$-supported Ziegler catalyst in the absence or presence of an internal or external electron donor so that the effects and roles of the electron donors could be clarified. The results showed that various kinds of active sites with different isospecificities, including the highest isospecific active sites responsible for producing the highest isotactic fraction (elution temperature: > 112°C) existed, even in the electron donor-free catalyst system. The isospecificity of the active sites in the donor-free catalyst might have originated from a surface monolayer multinuclear titanium species, namely an " island " of titanium species. The addition of the external electron donor converted a part of the aspecific and/or low isospecific active sites into the second highest isospecific active sites, but showed no effect on the formation of the highest isospecific active sites, whereas the addition of an internal donor played an important role in creating the highest isospecific active sites as well as suppressing the formation of the aspecific active sites.

Introduction

The elucidation of many unanswered questions about olefin polymerization with Ziegler catalyst is still an intensive research target from both the industrial and scientific aspects.[1, 2] The following subjects concerning the active sites are of particular interest in the discussion of the catalyst and polymerization: the formation and the deactivation of active sites, the structure and variation of the active sites, as well as their correlation to the catalyst

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performance. Although all these factors play crucial roles in determining the catalyst's performance, the comprehension of these fundamental subjects has progressed more slowly than the industrial development of the catalysts. A deeper understanding of the basic aspects is necessary for further developments in this area.

Based on these consideration, our attention has focused on the evaluation of the distribution states of the isospecific active sites formed in the catalysts and the effects and roles of the electron donor compounds on the isospecificity distribution. The distribution states of the isospecific active sites were derived from the isotacticity distribution of the polypropenes analyzed by the temperature rising elution fractionation (TREF) method.[3,4] A kinetic study to analyse the properties of the isospecific active sites was also considered, to provide a further insight into the nature of the isospecific active sites on the $MgCl_2$-supported Ziegler catalysts. This work was carried out as one of a series of efforts of our good understanding of stereospecific olefin polymerization by Ziegler catalysts, utilizing the unique advantages of the stopped-flow techniques.[5-12]

Experimental

Materials: Research grade propene donated by Tokuyama Corp. was used without further purification. $MgCl_2$ and cyclohexylmethyldimethoxysilane (CMDMS) were kindly supplied by Toho Titanium Co., Ltd. Ethylbenzoate (EB) and dibutylphthalate (DBP) were purchased from Wako Pure Chemical Industries, Ltd.. EB, DBP and CMDMS were dried over 13X molecular sieves. Triethylaluminum (TEA) was kindly donated by Tosoh Akzo Corp. TEA, EB, DBP and CMDMS were used as their toluene solutions. Heptane and toluene were purified by passing them through a 13X molecular sieve column.

Catalyst preparation: The internal electron donor-free $MgCl_2$-supported catalyst was prepared as follows. $MgCl_2$ ($11 m^2/g$; 36 g), $TiCl_4$ (108 ml), and heptane (108 ml) were placed in a 1.2 L stainless steel vibration mill pot with 55 balls (25 mm diameter) under nitrogen and ground for 30 h at room temperature. The ground product (200 ml) was treated with $TiCl_4$ (200 ml) in a 1 L three-necked flask at 90 °C for 2 h with stirring under nitrogen, followed by several washings with heptane and finally stored as a toluene slurry before polymerization. The Ti content of the catalyst was 2.2 wt.%. Two other internal-donor-containing $MgCl_2$-supported catalysts were prepared using a similar procedure except that the internal donor, EB or DBP, was used instead of $TiCl_4$ in the first ball-milling step. The Ti contents were 2.2 wt.%

and 2.4 wt.% for the $TiCl_4/EB/MgCl_2$ and $TiCl_4/DBP/MgCl_2$ catalysts, respectively.

Propene polymerization and estimation of kinetic parameters: The stopped-flow polymerization of propene and estimation of the kinetic parameters were carried out according to a previously reported method.[7,13-15] The propene polymerization was typically performed with the catalyst (ca.1.0 g) and TEA (14 mmol, Al/Ti molar ratio = 30) in toluene at 30 °C for 0.15 s. The toluene slurry (100 ml) of the catalyst and TEA solution in toluene (100 ml), saturated by propene (1 atm), were placed in two separate vessels. When using an external electron donor, EB or CMDMS was introduced into one of the vessels with the catalyst or with TEA.

The propagation rate constant (k_p) and active site concentration ([C*]) were determined by the following equations:

$$\overline{M}_n = M_0 \cdot \frac{k_p \cdot [M] \cdot t}{1 + k_{tr} \cdot t} \qquad (1)$$

$$Y = k_p \cdot [M] \cdot [C^*] \cdot t \qquad (2)$$

where $\overline{M}_n$, M_0, [M], t, and k_{tr} are the number-average molecular weight of the polymer, the molecular weight of the monomer, the monomer concentration, the polymerization time, and the transfer rate constant, respectively.

TREF method: The isotacticity distribution of the polypropenes (PPs) obtained in this study was determined by TREF (Senshu SSC-7300) using *o*-dichlorobenzene (ODCB) as the extraction solvent. Approximately 1.4 g of polymer was dissolved in 70 ml of ODCB at 140 °C. A part of the solution (50 ml, ca. 20 mg/ml) was eluted through the fraction column. The column was then slowly cooled to 20 °C (6.7 °C /h). Elution with ODCB (150 ml / h) was first carried out at 20 °C for 30 min to obtain the ODCB-soluble fraction, and then the column was heated to 140 °C at 10 °C / h.

GPC and ^{13}C-NMR: The molecular weight of the obtained polymer was determined by gel permeation chromatography (GPC, Senshu SSC-7100) using polystyrene gel columns (Tosoh

TSK-GEL G3000HHR and TSK-GEL G5000HHR) at 140 °C with *o*-dichlorobenzene as the solvent. The ^{13}C NMR spectra were recorded on a Varian Gemini-300 spectrometer at 120 °C using a 20 % (w/v) solution of 1,2,4-trichlorobenzene. Ten-percent (v/v) benzene-d^6 was added as an internal lock and hexamethyldisiloxane was used as a reference for the internal chemical shift.

Results and Discussion

Effect of addition of external electron donor

Table 1 shows the kinetic results and the stereoregularity obtained from the overall polymer prepared by the stopped-flow method in the absence or presence of an external electron donor (EB or CMDMS) with the internal electron donor-free $MgCl_2$-supported Ziegler catalyst. The results obtained from the stopped-flow polymerization are expected to provide important information on the effects and roles of the external electron donor with respect to the nature of the active sites just after their formation. With the addition of the external electron donor, increases in k_p, decreases in [C*], and improvements in the stereoregularity were observed.

Table 1. Results of stopped-flow propene polymerization[a)]

External Donor	$k_{p,iso}$ (L/mol s)	[C*] (mol%)	*mmmm*[b)] (mol%)
-	1380	9.9	57.2
EB	1790	5.6	62.6
CMDMS	1920	4.5	74.4

a) Polymerization condition: Al/Ti molar ratio = 30, Al/donor molar ratio = 20, temp. = 30 °C time = 0.15 s.
b) Determined by ^{13}C NMR

The isospecificity distributions of the active sites were also investigated utilizing the TREF method. The TREF diagrams of these polymers are shown in Figure 1. Characteristic TREF patterns showing three main peaks were obtained, indicating that each polymer possesses an isotacticity distribution which should be due to the existence of the isospecificity distribution of the active sites. With the addition of an external electron donor, an increase in the second highest isotactic fraction (elution temperature: 90 °C ~ 112 °C) and decrease in the atactic

fraction (elution temperature: < 20 °C) were induced, but the amount of the highest isotactic fraction (elution temperature: > 112 °C) remained unchanged (see Figures 1 (b) and (c)).

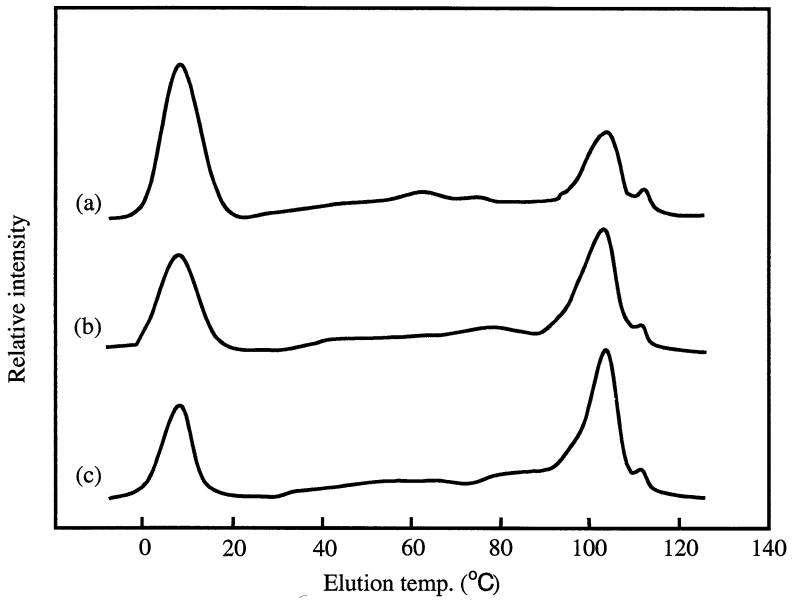

Fig. 1 TREF diagrams of PPs produced with an internal electron donor-free $MgCl_2$-supported Ziegler catalyst: (a) in the absence of electron donors, (b) in the presence of EB as the external electron donor, and (c) in the presence of CMDMS as the external electron donor.

Table 2 shows the kinetic results obtained from the second highest isotactic fractions (elution temperature: 90 °C ~ 112 °C). The increase in [C*] of the second highest isotactic fraction indicates that with the addition of an external electron donor, a part of the aspecific and/or low isospecific active sites were converted into the second highest isospecific active sites.

Table 2. Characterization of the second highest isotactic fraction[a] of PPs and kinetic parameters

External Donor	Yield (g/mol-Ti)	$\overline{M}_n$[b]	$\overline{M}_w/\overline{M}_n$[b]	*mmmm*[c] (mol%)	$k_{p,iso}$ (L/mol s)	[C*$_{iso}$] (mol%)
-	118	18700	1.8	94.6	4170	0.63
EB	146	21000	1.9	95.7	4680	0.69
CMDMS	173	21600	1.8	95.8	4830	0.80

a) Elution temperature: 90 °C ~ 112 °C
b) Determined by GPC
c) Determined by ^{13}C NMR

Table 3 shows the kinetic results obtained from the highest isotactic fractions (elution temperature: > 112 °C) of the resulting polymers. The important point is that the highest isospecific active sites corresponding to the highest isotactic fraction also exist in the electron donor-free catalyst system.

Table 3. Characterization of the highest isotactic fraction[a] of PPs and kinetic parameters

External Donor	Yield (g/mol-Ti)	$\overline{M}_n$[b]	$\overline{M}_w/\overline{M}_n$[b]	*mmmm*[c] (mol%)	$k_{p,iso}$ (L/mol s)	[C*$_{iso}$] (mol%)
-	16.7	41600	1.8	98.5	9300	0.041
EB	16.4	41700	1.7	98.4	9300	0.039
CMDMS	16.2	41500	1.7	98.6	9270	0.038

a) Elution temperature: over 112 °C
b) Determined by GPC
c) Determined by ^{13}C NMR

With the addition of an external electron donor, k_p and the meso pentad fraction of the polymers were increased. However, all the values obtained from the highest isotactic fraction (elution temperature: > 112 °C), such as the yield, $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, the meso pentad fraction, k_p and [C*], were almost constant, which means that no effects exist on the highest isospecific active sites with the addition of an external electron donor. With the addition of an external electron donor, transformation of the active sites from aspecific to isospecific was achieved, but the transformed isospecific active sites cannot produce polypropene with the highest

isotacticity. This coincides with the evidence shown in Figure 1, i.e., the obvious increase in the intensity of the second highest isotactic fraction and no change in the intensity of the highest isotactic fraction after the addition of the external donor.

Effect of addition of internal electron donor

In order to investigate the effects and roles of the internal electron donor, the stopped flow polymerization was performed using a $MgCl_2$-supported Ziegler catalyst with or without an internal electron donor (EB or DBP) in the absence of the external electron donor. With the addition of the internal electron donor, significant improvements in the stereoregularity were observed. The meso pentad fraction of the polypropene increased from 57.2% to 92% for EB and to 94% for DBP.

The TREF diagrams of these polymers are shown in Figure 2. With the addition of the internal donor, the atactic fraction (elution temperature: < 20 °C) and the second highest isotactic fraction (elution temperature: 90 °C ~ 112 °C) were substantially decreased, whereas the intensity of the highest isotactic fraction (elution temperature: > 112 °C) was drastically increased. This result clearly indicates that the internal donor plays an important role in generating the highest isospecific active sties as well as suppressing the formation of the aspecific and the second highest isospecific active sites.

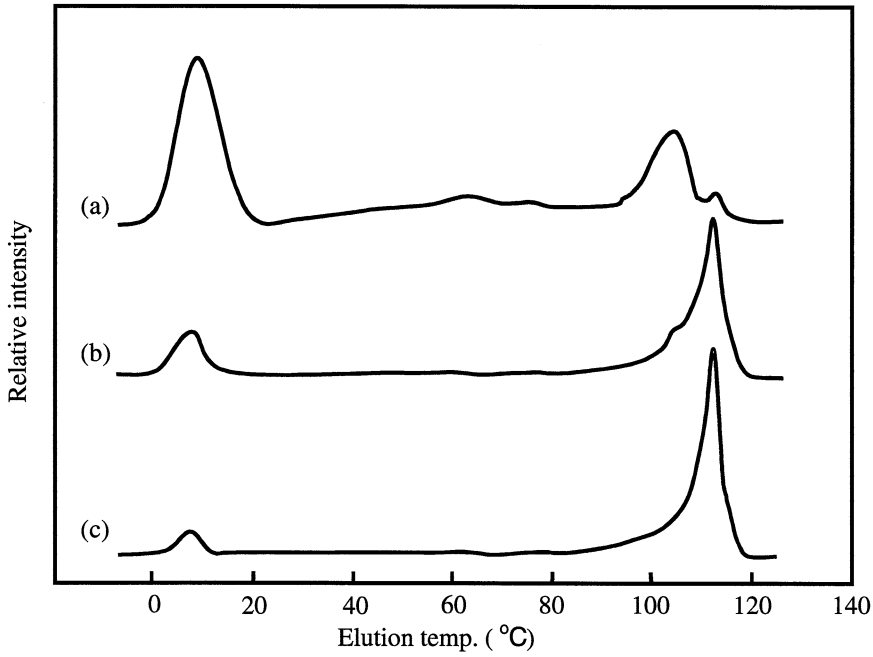

Fig. 2 TREF diagrams of PPs produced with $MgCl_2$-supported Ziegler catalyst: (a) in the absence of electron donors, (b) in the presence of EB as the internal electron donor, and (c) in the presence of DBP as the internal electron donor.

"Island" Model

The TREF results indicate that even the donor-free catalyst has an isospecificity distribution, which means that different kinds of active sites, including the highest isospecific active sites, are formed by Ti, Mg and Cl atoms without an internal or external electron donor. One possible model for the origin of the isospecificity distribution is the "surface monolayer multinuclear titanium species", namely an "island" of titanium species (see Figure 3).[16] In the "island", the isospecificity of active sites might be created by the steric structure of the atoms adjacent to the active Ti species, which is considered to be efficient enough to generate the highest isospecific active sites without an electron donor. The clear difference in the roles between the internal and external electron donors, that is, the internal donor can contribute to the formation of the highest isospecific active sites but the external donor cannot, indicates

that the internal donor has a stronger effect on the nature of the active sites in the "island". Since the internal electron donor may have a chance to interact with various catalyst components, such as titanium species in the " islands " and the $MgCl_2$ surface as shown in Figure 3, the steric hindrance of the internal electron donor, which coordinates to the Ti species adjacent to the active site in the "island", may more efficiently generate the highest isospecific active sites. Internal electron donor compounds coordinated on the "island" are also expected to suppress any change in the structure and property of the "island" which results from the migration of Cl atoms through the vacant sites produced by the attack of the alkylaluminum during polymerization.

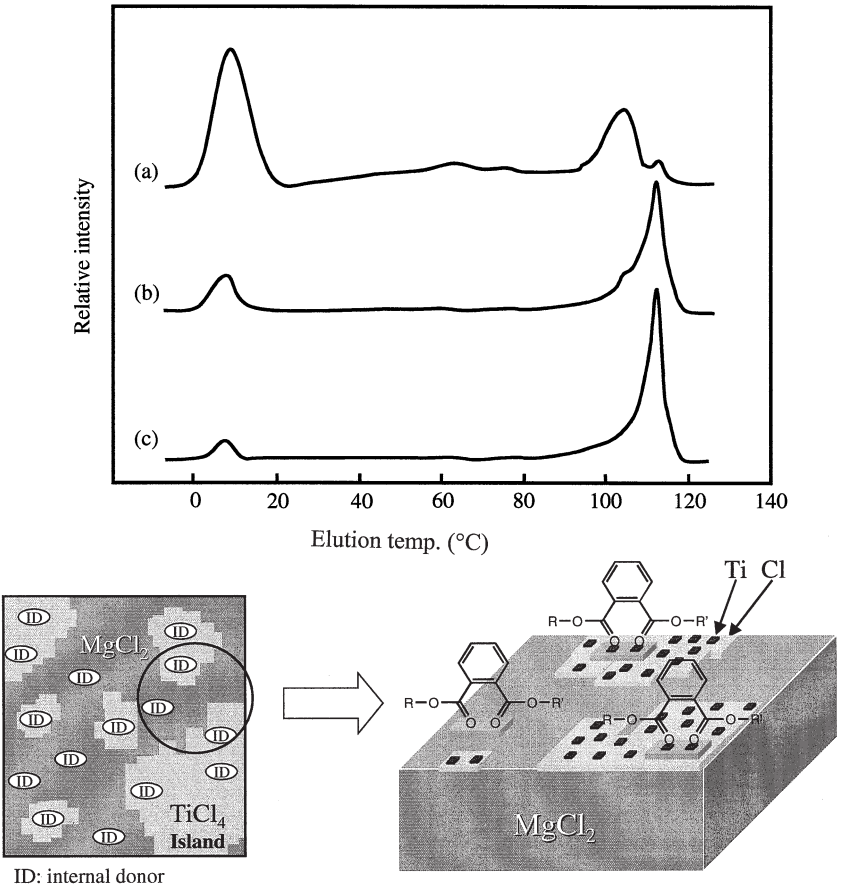

Fig. 3 "Island model": An "island" of Ti species and the states of the internal donor on the surface of the Ziegler catalyst.

Conclusions

The highest isospecific active sites corresponding to the highest isotactic polymer fraction in the TREF diagram exist even in the electron donor-free catalyst system. The isospecificity of active sites in the donor-free catalyst might originate from a surface monolayer multinuclear titanium species, namely an " island " of titanium species. Addition of the external electron donor converted a part of aspecific and/or low isospecific active sites into the second highest isospecific active sites but did not generate the highest isospecific active sites, whereas the internal electron donor played an important role in the formation of the highest isospecific active sites. The results obtained in this study clearly indicate the importance of the internal electron donor compared to the external donor. These resultants are of great significance for the design of the next generation Ziegler catalysts.

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