

Article

Precise Active Site Analysis for $\text{TiCl}_3/\text{MgCl}_2$ Ziegler-Natta Model Catalyst Based on Fractionation and Statistical Methods

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Received: 17 December 2012; in revised form: 30 January 2013 / Accepted: 1 February 2013 /
Published: 7 February 2013

Abstract: In heterogeneous Ziegler-Natta catalysts for olefin polymerization, isolation of a single type of active sites is a kind of ambition, which would solve long-standing questions on the relationship between active site and polymer structures. In this paper, polypropylene produced by $\text{TiCl}_3/\text{MgCl}_2$ model catalysts with minimum Ti heterogeneity was analyzed by combined solvent fractionation and the two-site statistical model. We found that the active sites of the model catalysts were classified into only three types, whose proportions were dependent on the Ti dispersion state. The addition of external donors not only newly formed highly isospecific sites, but also altered the stereochemical nature of the other active sites.

Keywords: Ziegler-Natta catalysts; propylene polymerization; model catalyst; active site; two-site model analysis

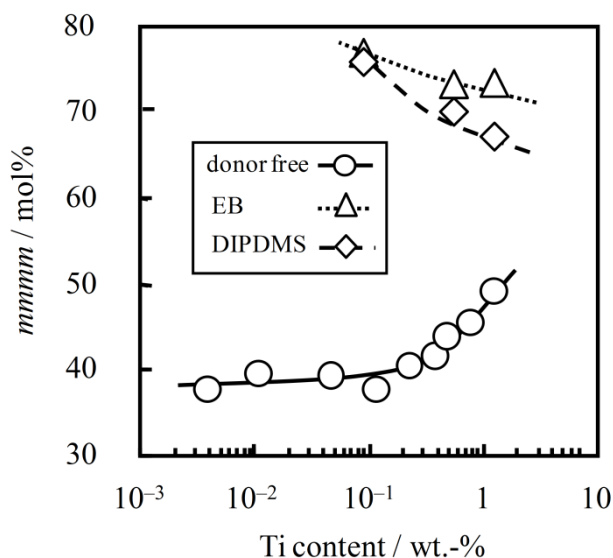
1. Introduction

Heterogeneous Ziegler-Natta catalysts are dominantly responsible for the industrial production of polypropylene (PP), due to their high activity, high isospecificity, superior morphology and broad molecular weight distribution (MWD) of produced PP. The catalysts are generally composed of a solid component ($\text{TiCl}_4/\text{MgCl}_2$ /internal donor) and an activator component (alkylaluminum/external donor). Alkylaluminum activates TiCl_4 through reduction and alkylation to initiate polymerization. The high

reactivity of alkylaluminum also causes the deactivation of catalysts, which go through the overreduction and agglomeration of Ti species [1–4], as well as the removal of donor molecules from surfaces. Consequently, Ti species are situated in various environments in terms of the oxidation state, dispersion and interaction with donors, which has prevented the understanding of the catalysts.

Recently, we have reported the influences of the Ti dispersion state on propylene polymerization performances using $\text{TiCl}_3/\text{MgCl}_2$ model catalysts with controlled Ti dispersion states [5–7]. In brief, the model catalysts were prepared by treating $\text{TiCl}_3 \cdot 3\text{pyridine}$ with diethylaluminum chloride (DEAC) in the presence of milled MgCl_2 . Thus, supported TiCl_3 molecules are much less mobile than TiCl_4 , enabling us to control and retain the Ti dispersion state through the Ti content. A lower Ti content results in less interacting or more isolated TiCl_3 molecules, while a higher Ti content leads to more interacting or more agglomerated species. Figure 1 reports the summary of our recent publication on the influences of the Ti contents on the propylene polymerization performances and on the efficiency of donors as a stereoselectivity modifier [6]. In the absence of donors, the stereoregularity of produced PP, *i.e.*, the catalyst stereospecificity exhibits two different dependences on the Ti content. Below 0.1 wt-%, the *mmmm* value became constant at around 37 mol%, indicating that the interaction between TiCl_3 molecules disappears and each molecule becomes isolated. Above 0.1 wt-%, the *mmmm* value monotonously increased from 37 to 50 mol%, which corresponds to the formation of TiCl_3 multinuclear species [8,9]. The other properties, such as the polymerization activity and MWD, follow the same dependences on the Ti content. Interestingly, the addition of donors increases the stereoregularity of PP most efficiently for the Ti mononuclear species with the lowest stereospecificity, which can be explained by the difficulty for donors to coadsorb around an active center for agglomerated Ti species. Temperature rising elution fractionation (TREF) experiments further revealed that poorly isospecific Ti mononuclear species were transformed into highly isospecific species, whose stereospecificity was different from that of the Ti species formed by agglomeration.

Figure 1. Stereoregularity of polypropylenes (PPs) produced by $\text{TiCl}_3/\text{MgCl}_2$ model catalysts as a function of the Ti content with and without donors. Propylene polymerization at normal pressure was conducted at 30 °C in heptane with $1.25 \text{ mmol} \cdot \text{L}^{-1}$ of triethylaluminum for 30 min.



Two types of fractionation approaches have been frequently employed in order to separate the contributions of different active sites to whole polymers. One is the solvent fractionation based on Soxhlet extraction using solvents having different boiling points or temperature-gradient fractionation techniques, such as TREF and CRYSTAF [10,11]. Both of these techniques fractionate PP mainly according to the melting temperature, which reflects the stereoregularity of the fractions. The other is statistical analysis based on numerical analyses of stereosequences of produced PP that is determined by ^{13}C -NMR. In a two-site model proposed by Doi *et al.* [12], stereosequences are fit to a theoretical equation, which supposes the existence of two types of active sites, respectively, based on enantiomorphous-site (ES) control and chain-end (CE) control statistics. Busico *et al.* [8] proposed a more sophisticated three-site model combined with high magnetic-field ^{13}C NMR, where the fitting quality was greatly improved by the addition of the third site based on the defective chain migratory mechanism to the two-site model. The three-site model requires longer sequences, such as heptad, due to the larger number of adjustable parameters, while the two-site model is more suitable to usual pentad sequences. It is notable that the three-site model was later updated by Terano *et al.* [9].

In this study, we have combined the model catalyst approach with the two types of the fractionation approaches, aiming at precise active site separation for Ziegler-Natta propylene polymerization catalysts to clarify the following issues:

- the origin of polydispersity of molecular weight—even though all Ti species were isolated below 0.1 wt%, the MWD value became 4–5, much larger than two for single-site catalysts [6];
- the difference of stereochemical features of active sites between isolated and agglomerated Ti species;
- detailed influences of donors on the stereochemical features of active sites and the reason why donors improved the stereospecificity of the Ti mononuclear species most efficiently [6].

PP produced by the $\text{TiCl}_3/\text{MgCl}_2$ model catalysts was first fractionated by boiling hexane and then subjected to statistical analysis based on the two-site model. It was found that active sites in the model catalysts could be represented by the following three types: ES1 site to produce hexane-insoluble (HI) isotactic PP at *mmmm* of 77 mol% with a minor fraction of weakly syndiotactic block, ES2 site to produce hexane-soluble (HS) isotactic PP at *mmmm* of 39 mol% and CE1 site to produce HS syndiotactic PP at *rrrr* of 38 mol%. The increase in the Ti loading, *i.e.*, more multinuclear Ti species, raised the proportion of the ES1 site with the reduction of the proportion of the ES2 site. In contrast, the proportion of the CE1 site remained constant. PP produced in the presence of ethyl benzoate (EB) as an external donor came from at least three types of new active sites, whose stereochemical natures were totally different from those in the absence of donors: two types of more isospecific sites and one type of more syndiospecific site. Mononuclear Ti species enhanced the formation of the most isospecific site in the presence of EB.

2. Experimental Section

$\text{TiCl}_3/\text{MgCl}_2$ model catalysts with a variety of Ti contents ranging from 0.011 to 1.3 wt% were prepared according to the previously reported procedure [5–7]. In brief, a specified amount of $\text{TiCl}_3 \cdot 3\text{Py}$ and milled MgCl_2 (donated by Toho Titanium Co., Ltd., a specific surface area of $65.1 \text{ m}^2 \cdot \text{g}^{-1}$) was reacted in the presence of DEAC (donated by Tosoh Finechem Corporation) at

Al/Ti = 78 mol·mol⁻¹ in *n*-heptane at r.t. for 3 h under N₂, followed by repetitive washing with *n*-heptane. PP was obtained using these catalysts. Polymerization was conducted in 100 mL *n*-heptane at 1 atm of propylene (supplied from Japan Polypropylene Corporation) flow for 30 min, where triethylaluminum (TEA, [Al] = 12.5 mmol·L⁻¹) was added prior to the injection of an appropriate amount of catalyst. Polymerization in the presence of EB (Al/EB = 10 mol·mol⁻¹) was also conducted. Thus, the obtained PP was washed with water, then reprecipitated from xylene with methanol and finally dried *in vacuo*.

The Soxhlet extraction was performed for a measured amount of PP using boiling *n*-hexane for 12 h. The soluble fraction was recovered by casting the resultant solution into methanol. The pentad stereosequences of PPs were analyzed by ¹³C NMR (Bruker 400 MHz NMR spectrometer) at 120 °C using 1,1,2,2-tetrachloroethane-*d*₂ as an internal lock and reference.

The two-site model [12] contains three adjustable parameters: σ = the probability to select a *d*-unit in the ES model, P_r = the probability to select a racemo diad configuration in the CE model and ω is the weight ratio between the ES and CE models. For example, meso pentad, *mmmm*, is expressed by:

$$mmmm = \omega\{\sigma^5 + (1 - \sigma)^5\} + (1 - \omega)(1 - P_r)^4 \quad (1)$$

The obtained pentad values were numerically fit to the theoretical equations with the above three parameters in order to minimize the sum of squares of errors (SSE), defined as:

$$SSE = \sum(\text{experimental pentad value} - \text{calculated pentad value})^2 \quad (2)$$

In most cases, the final SSE values were below 4. The error of pentad values could be 1.2 mol% at maximum, but was mostly within 0.6 mol%.

3. Results and Discussion

Before the fractionation using boiling hexane, the pentad stereosequences of whole PPs produced by the TiCl₃/MgCl₂ model catalysts with various Ti contents were determined by ¹³C NMR (Table 1). The obtained PPs were basically characteristic to isotactic PP produced based on the ES statistics: the largest proportion of *mmmm* with *rr*-type stereodefects (*i.e.*, *mmmr* $\approx$ *mmrr*). On the other hand, the observed *rrrr* values were always higher than those estimated from the ES statistics with the given *mmmm* values. These facts are typical characteristics of PP produced by Ziegler-Natta catalysts, which indicates the coexistence of the ES and CE statistics. Interestingly, the increase of the Ti content in the model catalysts not only led to increase in the *mmmm* value, but also accompanied a slight increase in the *rrrr* value, suggesting that both of the ES and CE natures were emphasized at higher Ti contents.

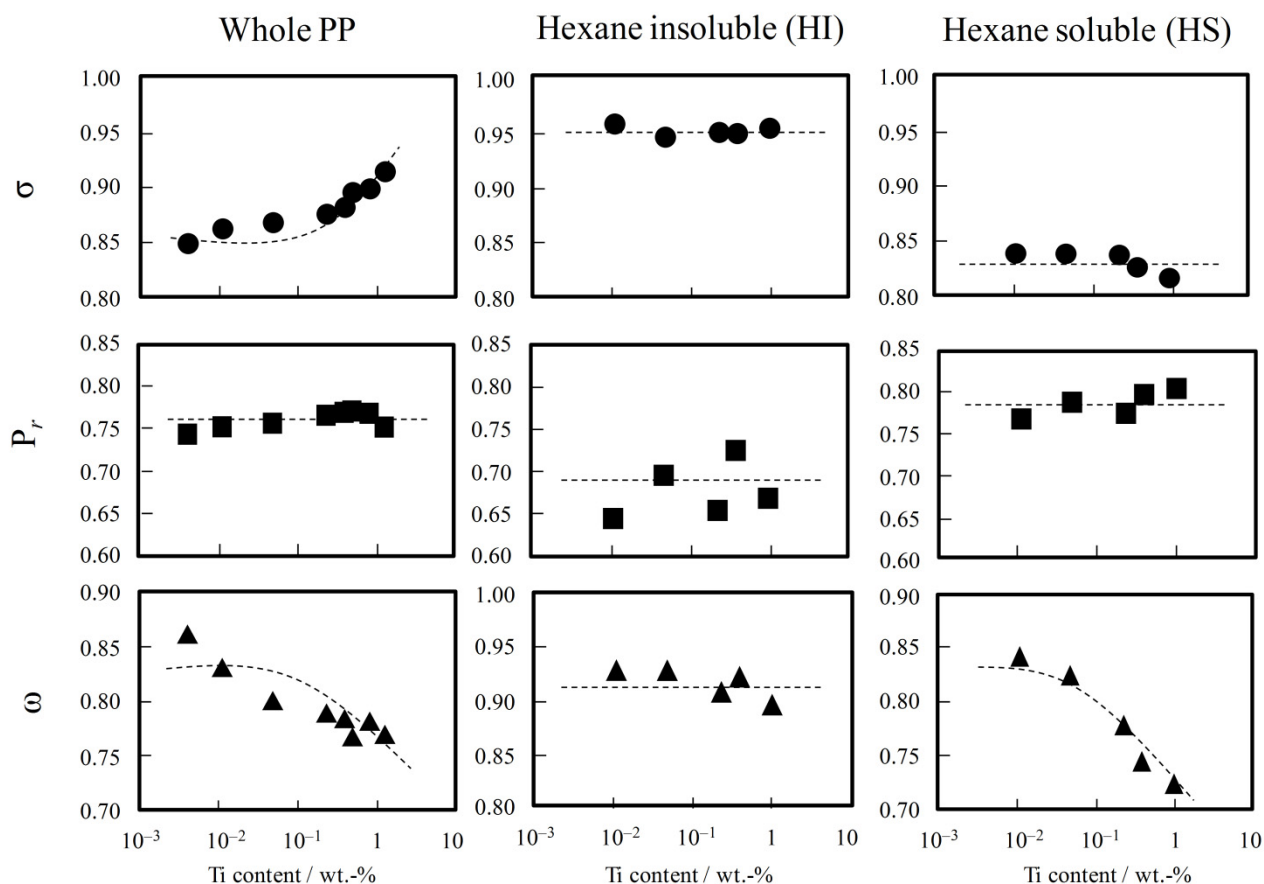
The pentad stereosequences of the whole PPs were analyzed based on the two-site model. The fitted parameters are plotted against the Ti content in Figure 2. Consistently with our previous conclusion that all of the Ti species became isolated mononuclear ones below 0.1 wt% of the Ti content, the three parameters converged below 0.1 wt%: σ around 0.86, P_r around 0.76 and ω around 0.83. The increase of the Ti content above 0.1 wt% built up σ while diminishing ω , thus explaining the increases of the *mmmm* and *rrrr* values at a higher Ti content. The dependence of the σ value on the Ti content suggested the presence of at least two types of ES sites, whose stereospecificities were different from each other. The constant P_r value suggested the dominance of one type of CE site.

Table 1. Pentad stereosequences (in mol%) and fitting results for whole PPs ^a.

	No donor								EB ^b	
Ti content/wt-%	0.004	0.011	0.048	0.23	0.39	0.49	0.81	1.3	0.092	1.26
<i>mmmm</i>	37.6	39.3	39.1	40.2	41.4	43.8	45.4	48.9	80.9	71.1
<i>mmmr</i>	13.9	12.4	12	11.1	11.5	10.5	11.8	9.6	3.2	5.2
<i>rmmr</i>	3.8	2.8	3	3.2	3.4	3	3.3	2	1.2	1.6
<i>mmrr</i>	14.4	14.6	13.5	13.3	12.1	11.6	10.3	10.7	5	6.2
<i>mmrm/rrmr</i>	8.2	7.9	8.3	7.5	7.5	7.4	7.1	7.1	2.1	3.5
<i>mrmr</i>	3.4	3.3	3.2	3.2	3.2	2.9	3.1	2.3	1.1	1.2
<i>rrrr</i>	5.6	6.6	7.6	8.2	8.4	8.9	8.2	7.8	2.6	4.8
<i>mrrr</i>	5.9	6.1	6.2	6.3	6.1	5.9	5.6	5.7	1.6	1.9
<i>mrrm</i>	7.3	7	7.1	6.9	6.6	6.1	5.3	5.8	2.2	3.5
σ	0.848	0.861	0.867	0.875	0.881	0.894	0.898	0.913	0.978	0.964
P_r	0.744	0.753	0.757	0.767	0.77	0.772	0.769	0.753	0.718	0.756
ω	0.861	0.831	0.801	0.789	0.784	0.768	0.782	0.77	0.905	0.853

^a Propylene polymerization at normal pressure was conducted at 30 °C in heptane with 1.25 mmol·L⁻¹ of triethylaluminum for 30 min. ^b EB was added as an external donor at Al/donor = 10.

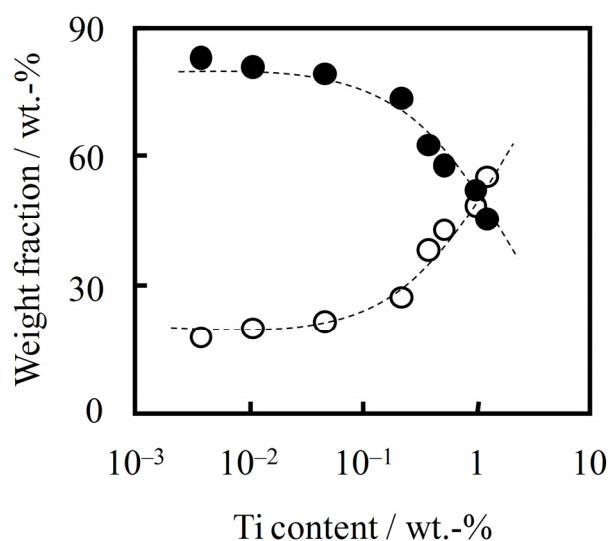
Figure 2. Fitting results of the two-site model for the pentad stereosequences of PPs produced by the model catalysts at different Ti contents.



In order to separate the two types of ES sites, PPs were fractionated into HI and HS fractions. Their proportions are displayed in Figure 3. The variations of the proportions against the Ti content were completely in line with the above-mentioned findings, while it was surprising to have *ca.* 20 wt% of HI even below 0.1 wt% dominantly with the Ti mononuclear species. Hence, some sort of heterogeneity remained even after the Ti species became isolated, which was reminiscent of the MWD value around 4–5 below 0.1 wt% [6]. The pentad stereosequences of the HI and HS fractions, as well as the fitting results based on the two-site model, are summarized in Tables 2 and 3, respectively. The pentad values for the HI fraction hardly depended on the Ti content. On the contrary, the *rrrr* value remarkably increased at a higher Ti content, albeit of the reduction in *mmmm* for the HS fraction. Thus, the increase in *mmmm* at higher Ti contents for the whole PPs arose from a higher proportion of HI, while the increase in *rrrr* was explained by the enhanced syndiotactic nature of HS.

The fitted parameters plotted against the Ti content (Figure 2) show the invariance of the stereospecificities in both of the ES and CE statistics for both of the fractions. This fact indicates that the stereosequences of PPs for the model catalysts are now represented by four types (two for ES and the other two for CE) of active sites, whose proportions vary along the Ti content (above 0.1 wt%). In turn, the nature of active sites do not depend on the Ti content, which can be understood within the three-site model [8,9] in a way that the stereoregulating ligands are invariantly Cl irrespective of the Ti content.

Figure 3. Weight fractions ((○) hexane-insoluble [HI] and (●) hexane-soluble [HS]) after fractionation of PPs produced by the model catalysts at different Ti contents.



For the HI fraction, the σ , P_r and ω values were, respectively, around 0.95, 0.69 ± 0.04 and 0.92, independent of the Ti content, where the error range for P_r was relatively large due to the marginal fraction of the CE site. The HI fraction consisted of a moderately isotactic part (corresponding to *mmmm* of 77 mol%) with the ES statistics and a small portion of a poorly syndiotactic part with the CE statistics. The syndiotacticity estimated from the P_r values were around 23 mol% of *rrrr*, which was too low not to be dissolved in boiling hexane. The only way to explain the present results is to consider that the poorly crystalline syndiotactic sequence was built into the isotactic sequence in a blocky way. A similar conclusion was drawn by Martuscelli *et al.* and Busico *et al.* [13,14]. Consequently, we have concluded that the HI fraction came from only one type of active sites, termed as ES1, having dominant ES and marginal CE characters. The constant ω value was consistent with this conclusion. It is likely that occasional 2,1 insertion at active sites forms a hindering methyl branch at the C_α position to initiate consecutive 2,1 insertion (which is known to follow the CE statistics) until the recovery to the energetically more favored 1,2 insertion. The active sites producing the HI fraction below 0.1 wt% (Figure 3) corresponded to the same sites whose proportion increased as the Ti content became higher. In other words, the same type of active sites with those formed by the agglomeration of the Ti species existed even when the Ti-Ti interaction disappeared. Considering that the multinucleation of the Ti species brings Cl ligands at the stereoregulating positions [8,9], it is plausible that Ti mononuclear species are located in a similar environment, for example, on defective surfaces of $MgCl_2$.

Similarly to the HI fraction, σ and P_r were independent of the Ti content. However, the ω value became smaller as the Ti content increased. This suggested that the HS fraction consisted of two of the same types of active sites irrespective of the Ti content, whose proportion (ω) varied along the Ti content. The ES site, termed as ES2, had a lower isospecificity (corresponding to *mmmm* of 39 mol%) than the ES1 site (*mmmm* of 77 mol%). It was expected that the ES2 site might retain a CE nature, as well as is the case for the ES1 site, but the dominance of an CE site made it invisible. The CE site, termed as CE1, showed higher syndiospecificity than that accompanied by the ES1 site, but the level of the specificity was still poor (corresponding to *rrrr* of 38 mol%). It is notable that the P_r obtained

for the CE1 site was almost identical to that determined in the two site model analysis for the whole PPs, which meant that the observed syndiotactic fractions mostly came from the CE1 site.

Table 2. Pentad stereosequences (in mol%) and fitting results for hexane-insoluble (HI) fractions.

	No donor					EB	
Ti content/wt-%	0.011	0.048	0.23	0.39	1	0.092	1.26
<i>mmmm</i>	74.4	69.8	69.9	70.6	70.3	90.5	88.3
<i>mmmr</i>	7.3	8.9	8.4	8.2	7.5	3	3.6
<i>rmmr</i>	1.6	1.3	1.7	1.2	1.7	0.6	0.8
<i>mmrr</i>	7.5	8.1	7.8	8.2	7.4	2.8	3.1
<i>mrmr/rrmr</i>	2.2	2.7	2.8	2.7	2.9	0.6	1
<i>mrmm</i>	0.9	1.1	1.3	0.9	1.3	0.2	0.2
<i>rrrr</i>	1.5	2	2	2.4	2.3	0.4	0.8
<i>mrrr</i>	1.6	1.7	2.1	2.1	2.2	0.4	0.6
<i>mrrm</i>	3.1	4.3	4.1	3.8	4.3	1.4	1.7
σ	0.957	0.945	0.949	0.948	0.953	0.985	0.983
P_r	0.644	0.695	0.654	0.725	0.668	0.6	0.67
ω	0.927	0.927	0.907	0.921	0.895	0.974	0.964

Table 3. Pentad stereosequences (in mol%) and fitting results for hexane-soluble (HS) fractions.

	No donor					EB	
Ti content/wt-%	0.011	0.048	0.23	0.39	1	0.092	1.26
<i>mmmm</i>	33.4	33.7	31.5	27.9	25.7	39.2	29.9
<i>mmmr</i>	13.7	13.5	12.4	11.9	11.6	11.3	11
<i>rmmr</i>	3	2.5	2.9	3	2.9	2.3	2.9
<i>mmrr</i>	15.1	15.1	14.7	14.8	14.3	13.4	13.3
<i>mrmr/rrmr</i>	8.9	9.7	10	10.8	11.6	7.7	10
<i>mrmm</i>	3.5	3.1	3.3	3.3	3.5	2	3
<i>rrrr</i>	7	8.3	9.4	12	13.2	10.8	13.9
<i>mrrr</i>	7.3	7.3	8.3	9.2	9.6	6.7	8.1
<i>mrrm</i>	7.2	6.9	7.5	7	7.7	6.5	7.9
σ	0.837	0.836	0.835	0.824	0.814	0.87	0.837
P_r	0.768	0.788	0.775	0.797	0.805	0.824	0.83
ω	0.842	0.824	0.778	0.744	0.723	0.786	0.733

The unanswered issues (i) and (ii) for the active sites of the $\text{TiCl}_3/\text{MgCl}_2$ model catalysts were clarified by the combination of solvent fractionation and two-site model analysis. The results indicated that the stereochemistry is identical between the mononuclear and multinuclear Ti species, and the active sites were always represented by the following two types of ES sites and one type of CE site, whose proportion was dependent on the Ti content.

ES1: A moderately isospecific ES site with a marginal CE nature, whose proportion decreased at lower Ti contents, but never disappeared.

ES2: A poorly isospecific ES site, whose proportion decreased at the expense of the ES1 formation.

CE1: A poorly syndiospecific CE site, whose proportion was nearly constant.

The co-existence of these three types of active sites plausibly explains the MWD value around 4–5 even after the Ti species became isolatedly mononuclear below 0.1 wt%.

The stereostructures of the whole PPs produced in the presence of EB were analyzed by the two-site model for two representative Ti contents (0.092 and 1.26 wt% for the mononuclear and multinuclear Ti species, respectively). The fitting results are shown in Table 1. Compared with the results in the absence of donors, both of the σ and ω values increased, while the P_r values were not largely changed. Thus, the addition of EB enhanced the isospecific ES nature of active sites. The σ value became smaller for the multinuclear species in contrast to the results obtained in the absence of donors. This trend is in line with our previous conclusion that the conversion of active sites into more isospecific ones by donors occurs more efficiently for a lower Ti content.

The PPs obtained in the presence of EB were similarly fractionated and analyzed, whose results are shown in Tables 2 and 3 for the HI and HS fractions, respectively. For the HI fraction, the fitting results (*i.e.*, σ , P_r , ω) were hardly dependent on the Ti content (greater error range for P_r due to a very minor syndiotactic fraction). According to similar considerations for the HI fraction in the absence of donors, it was natural for us to conclude that the HI fraction came from only one sort of active site (termed as ES3) with dominant ES and minor CE characters. However, the performance of ES3 was clearly different from that of ES1: higher isospecificity (corresponding to *mmmm* of 92 mol%) with less and more poorly syndiotactic blocks (corresponding to *rrrr* roughly about 16 mol%). These results correspond to the formation of new isospecific active sites in the presence of donors.

For the HS fraction, not only ω , but also σ , values decreased for the higher Ti content. This result indicated that ES-type active sites for the HS fraction were not completely separated and remained a multisite character. On the other hand, the P_r value was kept constant, indicating the presence of dominant CE-type active sites. These active sites are respectively termed as ES4m and CE2. Note that the ES4m site contained at least two types of ES sites (multisite), whose proportion varied along the Ti content. The ES4m site exhibited a higher isospecificity than the corresponding ES2 site. It means that donors not only form highly isospecific sites, like ES3, but also induce some level of the specificity improvements for poorly isospecific sites. Briefly, donors affect Ti species in a non-uniform manner, where most of the active sites are converted into highly isospecific ones, but the remaining active sites are incompletely converted. CE2 had slightly improved (but still poor) syndiospecificity over CE1. The ω value decreased for the higher Ti content, similarly to the donor-free case. However, the absolute values became lower than the donor-free case, dictating that the addition of donors increases not only the syndiospecificity (higher P_r), but also the CE nature (lower ω), for the HS fraction.

We found that the addition of EB formed at least three types of active sites, whose performances were different from the three sites made in the absence of donors. The characteristics of the three sites are summarized below.

ES3: A highly isospecific ES site with a marginal CE nature. Its proportion increased for the Ti mononuclear species, which is why donors convert the mononuclear species more efficiently into highly isospecific sites. It was envisaged that the addition of donors might convert the ES2 site (the most dominant site for lower Ti contents) into the ES3 site.

ES4m: It contained at least two-types of isospecific ES sites, whose specificity was poor, but higher than that for ES2.

CE2: A poorly syndiospecific CE site, whose specificity was higher than that for CE1.

4. Conclusions

TiCl₃/MgCl₂ model catalysts with controlled dispersion of Ti species were applied for the purpose of enabling active-site analyses at the single-site level with the aid of solvent fractionation and two-site statistical analysis. In the absence of a donor, we have successfully separated active sites of the model catalysts into only three types: ES1, ES2 and CE1. The proportion of the moderately isotactic ES1 site increased along the Ti content, at the expense of the proportion of the poorly isospecific ES2 site, thus raising the isoregularity of the whole polymer. On the other hand, the poorly syndiospecific CE1 site always existed at the same proportion irrespective of the Ti content. Notably, even after the Ti content became sufficiently low in order to isolate each Ti species into a mononuclear, the contribution from the ES1 site remained in a non-negligible amount, which was likely attributed to Ti species located at defective MgCl₂ surfaces. The addition of EB newly formed highly isospecific sites was classified as ES3, which was more obvious for a lower Ti content. It was considered that the addition of a donor might convert the ES2 site more efficiently into the ES3 site. In addition, the other active sites formed in the presence of EB (ES4m, CE2) were different from those formed in the absence of a donor, suggesting that the addition of a donor totally changed the nature of the active surfaces. Thus, we have succeeded in analyzing the stereochemical nature of active sites at the single-site level using a novel model catalyst approach and in extracting valid mechanistic aspects on active sites of Ziegler-Natta catalysts.

References

1. Albizzati, E.; Giannini, U.; Collina, G.; Noristi, L.; Resconi, L. In *Polypropylene Handbook*; Moore, E.P., Ed.; Hanser: New York, NY, USA, 1996.
2. Kashiwa, N.; Yoshitake, J. The influence of the valence state of titanium in MgCl₂-supported titanium catalysts on olefin polymerization. *Makromol. Chem.* **1984**, *185*, 1133–1138.
3. Poluboyarov, V.A.; Anufrienko, V.F.; Zakharov, V.A.; Sergeev, S.A.; Makhtarulin, S.I.; Bukatov, G.D. ESR studies of the state of Ti³⁺ and Ti²⁺ in Ti–Mg catalysts for olefin polymerization. *React. Kinet. Catal. Lett.* **1984**, *26*, 347–351.
4. Taniike, T.; Wada, T.; Kouzai, I.; Takahashi, S.; Terano, M. Role of dispersion state of Ti species in deactivation of MgCl₂-supported Ziegler-Natta catalysts. *Macromol. Res.* **2010**, *18*, 839–844.
5. Kouzai, I.; Liu, B.; Wada, T.; Terano, M. Effects of Hydrogen for Different Stereospecific Active Sites on Ultra Low TiCl₃ Loading Supported Catalyst. *Macromol. React. Eng.* **2007**, *1*, 160–164.
6. Wada, T.; Taniike, T.; Kouzai, I.; Takahashi, S.; Terano, M. Propylene Polymerization performance of isolated and aggregated ti species studied using a well-designed TiCl₃/MgCl₂ Ziegler-Natta model catalyst. *Macromol. Rapid. Commun.* **2009**, *30*, 887–891.
7. Taniike, T.; Takahashi, S.; Wada, T.; Kouzai, I.; Terano, M. Effects of molecular dispersion state of surface Ti species on ethylene-propylene copolymerization with TiCl₃-based Ziegler-Natta model catalyst. *Macromol. Res.* **2010**, *18*, 834–838.

8. Busico, V.; Cipullo, R.; Monaco, G.; Talarico, G.; Vacatello, M. High-resolution ^{13}C NMR configurational analysis of polypropylene made with MgCl_2 -supported Ziegler–Natta catalysts. 1. the “model” system $\text{MgCl}_2/\text{TiCl}_4$ –2,6-dimethylpyridine/ $\text{Al}(\text{C}_2\text{H}_5)_3$. *Macromolecules* **1999**, *32*, 4173–4182.
9. Liu, B.; Nitta, T.; Nakatani, H.; Terano, M. Specific roles of Al-Alkyl cocatalyst in the origin of isospecificity of active sites on donor-free $\text{TiCl}_4/\text{MgCl}_2$ Ziegler-Natta catalyst. *Macromol. Chem. Phys.* **2003**, *203*, 2412–2421.
10. Mingozi, I.; Cecchin, G.; Morini, G. Tacticity Distribution of Polypropene by Preparative and Analytical Temperature-Rising Elution Fractionation (TREF). *Int. J. Polym. Anal. Charact.* **1997**, *3*, 293–317.
11. Kissin, Y.V.; Fruitwala, H.A. Analysis of polyolefins and olefin copolymers using Crystaf technique: Resolution of Crystaf curves. *J. Appl. Polym. Sci.* **2007**, *106*, 3872–3883.
12. Inoue, Y.; Itabashi, Y.; Chujo, R.; Doi, Y. Studies of the stereospecific polymerization mechanism of propylene by a modified Ziegler-Natta catalyst based on 125 MHz ^{13}C NMR spectra. *Polymer* **1984**, *25*, 1640–1644.
13. Martuscelli, E.; Avella, M.; Segre, A.L.; Rossi, E.; Drusco, G.D.; Galli, P.; Simonazzi, T. Stereochemical composition-properties relationships in isotactic polypropylenes obtained with different catalyst systems. *Polymer* **1985**, *26*, 259–269.
14. Busico, V.; Cipullo, R.; Corradini, P.; De Biasio, R. Propene polymerization in the presence of MgCl_2 -supported Ziegler-Natta catalysts, 5. Microstructural characterization of the “isotactic” (heptane-insoluble) polypropene fractions. *Macromol. Chem. Phys.* **1995**, *196*, 491–498.