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Formation, deactivation and transformation of stereospecific active sites on $TiCl_4$/dibutylphthalate/$Mg(OEt)_2$ catalyst induced by short time reaction with Al-alkyl cocatalyst

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Abstract

Formation, deactivation and transformation of stereospecific active sites on $TiCl_4$/dibutylphthalate (DBP)/$Mg(OEt)_2$ Ziegler–Natta catalyst induced by short time reaction with triethylaluminum (TEA) cocatalyst (with TEA pretreatment time from 0 to 600 s) were investigated by stopped-flow propene polymerization combined with temperature rising elution fractionation (TREF) and GPC methods. It was demonstrated that both formation and deactivation of active sites with broad multiplicity in isospecificity on the catalyst are slow reactions with an induction period of ca. 0.2 s. It was most important to find that the formation of active sites with the highest isospecificity strongly depends on the interaction between the catalyst and cocatalyst (up to 60 s of pretreatment) even in the presence of internal donor. This newly observed phenomenon (according to our knowledge) suggested that the transformation of monometallic active sites (aspecific or less isospecific) into bimetallic active sites (highly isospecific) through reversible complexing with TEA cocatalyst (or its reaction product diethylaluminum chloride (DEAC)) in Ziegler–Natta catalysts cannot be overlooked even in the presence of internal electron donor. The existence of $-OC_2H_5$ ligand in the catalyst most probably gave birth to a new group of active titanium species. The stability of active sites increases with increasing isospecificity in the early stage of pretreatment (up to 60 s of pretreatment). While all the active sites became relatively stable in the later stage of pretreatment (from 60 to 600 s of pretreatment). The extraction of internal donor DBP by TEA from the catalyst within the pretreatment procedure is found to initiate from 60 s of pretreatment resulting in slight transformation of isospecific active sites into aspecific sites.

Keywords: Ziegler–Natta catalyst; Stereospecific active site; $TiCl_4$/dibutylphthalate/$Mg(OEt)_2$; Transformation; Stopped-flow propene polymerization

1. Introduction

The large-scale increasing production of polyolefins has been significantly enhanced by the development of highly efficient supported Ziegler–Natta catalysts. However, a complete understanding of these catalysts has not been achieved in spite of almost half a century of research efforts in this field. Particularly, the topics concerning the formation mechanism and nature of stereospecific active sites as well as the polymerization mechanism are still open for discussion, because direct characterization of the formation process and

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stereochemical state of active sites are very difficult during polymerization proceeds, and most of the information by now is solely derived from indirect experimental indications. The use of an Al-alkyl cocatalyst, such as triethylaluminum (TEA), as an activating agent is indispensable for olefin polymerization with Ziegler–Natta catalysts. It is generally accepted that the formation of active sites on Ziegler–Natta catalysts for olefin polymerization is accomplished through reduction and alkylation of surface titanium species by interaction of the catalyst with Al-alkyl cocatalyst [1]. The stereospecificity of the active sites formed after the interaction of the catalyst with Al-alkyl cocatalyst is known to be greatly affected by different types of cocatalysts [2]. Whereas, the specific mechanism on how the cocatalyst affects the formation process and physicochemical feature of stereospecific active sites has remained ambiguous. Moreover, the formation process of active sites resulted from the interaction between catalyst and cocatalyst is usually very fast and difficult to observe by usual methods. At the same time, the induction potential of the surface titanium species in the formation reaction of active sites may greatly depend on the type of catalyst as well as the surface heterogeneity of the catalyst [3–5]. This means that titanium species of potential active sites on different types of catalysts or on different surface location of the same type catalyst may exhibit different tendency in the formation of active sites. It would be most interesting if the formation tendency of active sites could also be correlated with the stereospecificity of these active sites. On the other hand, the active sites formed may suffer from deactivation due to over-reduction of active titanium species through its further contact with Al-alkyl cocatalyst during the polymerization process [6–9]. It is also important to remember the existence of non-uniform state of active sites, each type of which having different isospecificity may demonstrate different over-reduction potential, so to speak each type of active site with different stereospecificity is expected to have different tendency in the deactivation process as well.

For supported Ziegler–Natta catalysts, electron donor (Lewis base) is often employed as a necessary third component to improve the stereospecificity of the catalysts. Although many understandings have been achieved on the effects of electron donors, the specific mechanism still remained unclassified [2,10–15]. For example, how the existence of internal electron donor in the neighborhood of the surface titanium species of potential active sites would affect the formation, deactivation and transformation of stereospecific active sites after interaction with Al-alkyl cocatalysts is waiting for elucidation. Furthermore, the internal electron donor, which may affect both stereospecificity and reactivity of the active sites on internal donor contained-type catalysts, might be extracted by the Al-alkyl cocatalyst during the polymerization process [16–22]. How and when the extraction of internal electron donor from neighborhood of the active sites by the cocatalyst would affect the distribution state of stereospecific active sites are also important and interesting topics which we would like to deal with herein. In general, all the above-mentioned factors will surely result in the successive change of nature and distribution state of stereospecific active sites on the Ziegler–Natta catalysts in the whole polymerization process, which is very difficult to be investigated using a conventional method and seldom reported in the literature.

In this work, stopped-flow propene polymerizations using a supported Ziegler–Natta catalyst pretreated by TEA cocatalyst within a short period of time were utilized as model reactions for probing the mechanism concerning the dynamic successive formation, deactivation and transformation of stereospecific active sites on the catalyst in the presence of internal electron donor during the polymerization process. The stopped-flow polymerization using Ziegler–Natta catalysts within an extremely short period (ca. 0.2 s), which is much less than the average lifetime of the growing polymer chains, has been proven to be a quasi-living polymerization process. During the period, the states of the active sites are constant without time-dependent changes and any type of side reactions including chain transfer and deactivation after the initiation of polymerization can be negligible. The technique has been extensively applied to various kinds of investigations in heterogeneous Ziegler–Natta catalysis for studies on the nature of active sites and elucidation of the olefin polymerization mechanism [3,5,10,14,23–38]. The nature and distribution state of active sites on the catalysts derived from short time interaction with TEA cocatalyst can be studied through direct characterization of those polymers obtained in the method. Recently, we have demonstrated

that the combination of stopped-flow technique with temperature rising elution fractionation (TREF) and GPC methods provided an ideal method for substantial research on the stereospecific nature of active sites [10,30]. The concentration of active sites and chain propagation rate constant can be calculated based on GPC analysis of the polymer obtained. While, the distribution state of isospecificity of active sites on the catalysts can be derived from the isotacticity distribution of the polypropene analyzed by means of TREF method. As it is commonly assumed that the crystallinity of the polypropenes is mainly governed by isotacticity [13]. Recently, many reports have been published on TREF analysis, which is suitable for the determination of the microstructural heterogeneity of semicrystalline polyolefins [39–44]. TREF is a sophisticated system, by which the polymer samples having different crystallinity are separated at different temperature, and thus the distribution state of crystallinity of the polymer can be obtained. For polypropene, the distribution state of crystallinity is corresponding to its isotacticity distribution. However, the isotacticity distribution state cannot be directly correlated with the intrinsic state of isospecificity of active sites on Ziegler–Natta catalysts when the polypropene is produced from a conventional polymerization method (usually with long duration of polymerization time), because there exist time-dependent changes of the states of active sites and various unfavorable side reactions, such as chain transfer and deactivation, etc. and thus several hundreds or thousands of polymer chains are produced from each active site in a varying state during the whole conventional polymerization process. This problem can be completely overcome by using the stopped-flow polymerization method (usually with ca. ∼0.2 s polymerization time), in which each polymer chain is considered to be only produced from one active site, resulting in that the variation in the TREF profile of polypropenes obtained with the catalyst at different length of TEA pretreatment time directly reflect the time-dependent change in the nature and distribution state of isospecificity of the active sites. Therefore, the TREF method is implemented for the analysis of the polypropenes obtained by stopped-flow polymerization to achieve the distribution state of isospecificity of active sites on the catalyst under a TEA pretreatment procedure (with varying length of pretreatment time).

Generally, in this work, the dynamic successive formation, deactivation and transformation of stereospecific active sites on a supported Ziegler–Natta catalyst induced by TEA pretreatment had been studied by the combination of GPC, TREF and stopped-flow propene polymerization methods with respect to different length of pretreatment time. The modified stopped-flow system has been found to be most feasible in investigating the catalyst pretreatment effects induced by various reagents including Al-alkyl cocatalyst as well as developing novel block copolymers [10,14,29,32,33,35]. Substantially, using a modified stopped-flow system with three vessels, a first step of TEA pretreatment (0–600 s) to the catalyst ($TiCl_4$/DBP/$Mg(OEt)_2$) followed by a second step of propene polymerization (polymerization time is set at 0.15 s) can be precisely controlled. By varying the length of pretreatment time from 0 to 600 s, the dynamic reaction process during interaction between the catalyst and cocatalyst can be directly observed. The work is carried out as one of our serial efforts to elucidate the effects of Al-alkyl cocatalyst [10], electron donor [14,30,32,34,35], catalytic component and catalyst preparation method [5], etc. on the stereospecific polymerization of olefins by Ziegler–Natta catalysts utilizing the unique advantages of the stopped-flow techniques.

2. Experimental

2.1. Materials

Propene of research grade (donated by Chisso Corp.) was used without further purification. Dibutylphthalate (DBP, purchased from Wako Pure Chemical Industries Ltd.) was used as an internal electron donor after dehydration with molecular sieves. Anhydrous $Mg(OEt)_2$, $TiCl_4$ (both donated by Toho Titanium Co. Ltd.), triethylaluminum (donated by Tosoh Akzo Corp.) and nitrogen (purchased from Uno Sanso Co.) were used without further purification. TEA was used as heptane solution. Heptane was purified by passing through a molecular sieves 13X column.

2.2. Catalyst preparation

The performance of supported Ziegler–Natta catalysts is known to be drastically affected by the

preparation method as well as the property of each component used as raw material [3,5]. In this work, a diester-type catalyst $TiCl_4$/DBP/$Mg(OEt)_2$ was prepared by a chemical reaction method without mechanical treatment (e.g. ball milling). $TiCl_4$ was reacted with a mixture of $Mg(OEt)_2$ and DBP in the following procedure: $Mg(OEt)_2$ (10 g) and $TiCl_4$ (20 ml) in toluene (80 ml) were heated up to 90 °C, mixed with DBP (2.7 ml) and reacted at 115 °C for 2 h. The mixture was washed with toluene, and reacted again with $TiCl_4$ (20 ml) in toluene (80 ml) at 115 °C for 2 h. Finally, the catalyst obtained was washed with heptane for several times. Ti content was 0.54 mmol Ti/g_{cat}. The catalyst was used as heptane slurry.

2.3. Stopped-flow propene polymerization

As for the precise control of the short pretreatment time, a modified three-vessel-type stopped-flow apparatus (Fig. 1) was used [10,29]. The first step of catalyst pretreatment was carried out with TEA at Al/Ti molar ratio of 30 at 30 °C for different period of time ranging from 0.2 to 600 s followed by a second step of stopped-flow propene polymerization which was performed with the catalyst (0.47 mmol Ti) and 14 mmol of $Al(C_2H_5)_3$ (70 mmol/l, Al/Ti molar ratio = 30) in heptane at 30 °C. In all cases, the polymerization time was adjusted to be ca. 0.15 s. As shown in Fig. 1, the heptane slurry (100 ml) of the catalyst and $Al(C_2H_5)_3$ solution in heptane (100 ml) were placed in vessels A and B, respectively, while propene-saturated heptane (100 ml) was placed in vessel C. The pretreatment of the catalyst with TEA was conducted in the Teflon tube from point X to Y, followed by the stopped-flow propene polymerization in the part from point Y to Z. The pretreatment time can be accurately controlled between 0.2 and 10 s by changing the length of the Teflon tube from point X to Y. In case of the pretreatment beyond 10 s, it was performed in vessel A, whereas only heptane was introduced into vessel B. Heptane in vessel C was saturated with propene. When polymerization was conducted using catalyst without pretreatment, the TEA solution in heptane saturated with propene was placed in vessel C, while the catalyst slurry and heptane were placed in vessels A and B, respectively.

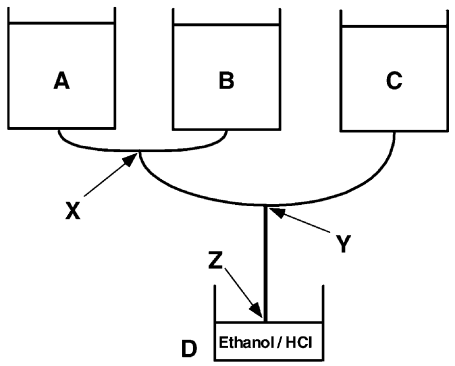


Fig. 1. Schematic illustration of the modified stopped-flow apparatus for TEA pretreatment and propene polymerization of the $TiCl_4$/DBP/$Mg(OEt)_2$ Ziegler–Natta catalyst (A–C: vessels with water jacket; D: ethanol with HCl as a quenching agent; X and Y: three-way Teflon taps).

2.4. GPC characterization of polypropenes

Molecular weight and molecular weight distribution of the polypropenes obtained in this study were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (Tosoh TSK-GEL G3000HHR and TSK-GEL G5000HHR) at 140 °C using *o*-dichlorobenzene (ODCB) as a solvent.

2.5. TREF analysis of polypropenes

Isotacticity distribution of the polypropenes obtained in this study was determined by TREF (Senshu SSC-7300) with ODCB as an extraction solvent, which contains 0.03 wt.% of 2,6-di-*tert*-butyl-*p*-cresol as an antioxidant. A fraction column packed with Chromosorb (bought from Celite Corp.) with 10 mm in diameter and 30 cm in length was used for the TREF characterization. About 70 mg of each polypropene sample was dissolved in 10 ml of ODCB at 140 °C, and a part of the solution (ca. 6 ml) was passed through the fraction column, which was slowly cooled down at 6.7 °C/h from 140 to 20 °C simultaneously. Elution of the deposited polymer with ODCB at a flow rate of 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 at 16 °C/h up to 140 °C. The eluted polypropene solution was analyzed by a refractive index detector to obtain the TREF profile.

3. Results and discussion

The relationship of yield, number average molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of the polypropenes obtained by stopped-flow polymerization versus the time period (0–600 s) of TEA pretreatment to the catalyst is shown in Table 1. As it can be seen, the catalyst shows quite low activity for the stopped-flow propene polymerization without TEA pretreatment, as well as with up to 0.2 s of TEA pretreatment. The activity was found to increase gradually from 2 to 10 s of TEA pretreatment and then to decrease from 10 to 60 s followed by a very slowly decreasing up to 600 s of TEA pretreatment. Accordingly, the number average molecular weight of the polypropenes gradually increases up to 60 s of pretreatment before reaching a plateau at ca. 3700–3800 in the later stage of TEA pretreatment (from 60 to 600 s of pretreatment). The molecular weight distributions of the polypropenes are broad and lying at 4.3–5.4 indicating a broad distribution state of active sites due to the TEA pretreatment. The change tendency of GPC curves of the polypropenes obtained with increasing length of TEA pretreatment time can also be observed in Fig. 2. As shown in Fig. 3, the variation tendency of active sites concentration [C^*] and chain propagation rate constant (k_p) versus the period of TEA pretreatment time take on the same tendency as the polymer yield and number average molecular weight versus the period of TEA pretreatment time, respectively. The facts mentioned above demonstrate that the formation of active sites on the catalyst after its contact with TEA cocatalyst proceeds slowly, and consequently these active sites just formed are relatively stable and mostly not so easily subject to deactivation during further contact with TEA cocatalyst under the pretreatment

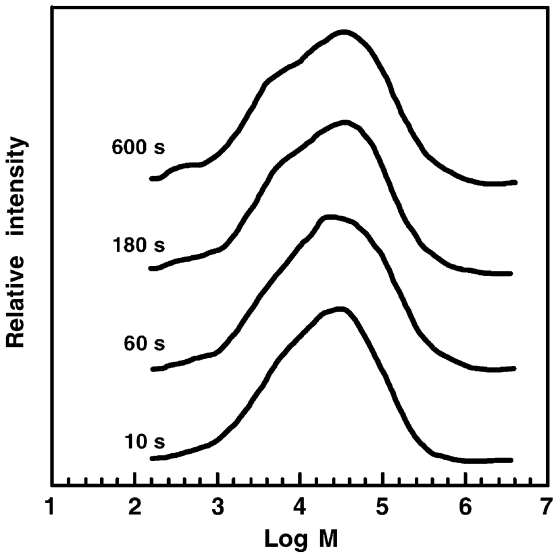


Fig. 2. Dependence of GPC curves on catalyst pretreatment time for polypropenes obtained in stopped-flow polymerization with the TEA-pretreated $TiCl_4$/DBP/$Mg(OEt)_2$ catalysts. TEA pretreatment time: 10, 60, 180 and 600 s.

Table 1
The relationship of yield, number average molecular weight ($\bar{M}_n$), molecular weight distribution ($\bar{M}_w/\bar{M}_n$) and weight fractions of polypropenes obtained in stopped-flow polymerization with the $TiCl_4$/DBP/$Mg(OEt)_2$ Ziegler–Natta catalyst at different TEA pretreatment times[a]

Pretreatment time (s)	Yield (g PP/mol Ti)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	Weight fraction[c] (%)			
				~20 °C	20–100 °C	100–110 °C	110–140 °C
0	ND[d]	–	–	–	–	–	–
0.2	Trace	–	–	–	–	–	–
2	15	2000	4.3	–	–	–	–
10	35	2800	4.7	24	40	29	7
60	30	3700	5.2	21	41	23	15
180	29	3800	4.6	30	32	24	14
600	28	3700	5.4	34	32	20	14

[a] The polymerization was carried out with TEA ([Al] = 70 mmol/l, Al/Ti = 30) in heptane at 30 °C for ca. 0.15 s after the pretreatment.
[b] Determined by GPC method.
[c] Fractionated by TREF method.
[d] Not detected.

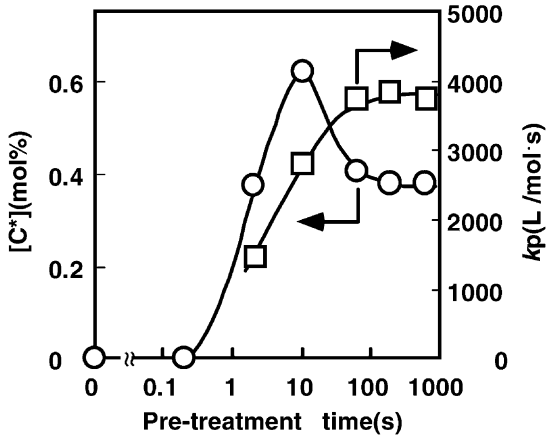


Fig. 3. Dependence of active sites concentration [C^*] (○) and chain propagation rate constant k_p (□) on catalyst pretreatment time in stopped-flow propene polymerization with the TEA-pretreated $TiCl_4$/DBP/$Mg(OEt)_2$ catalysts.

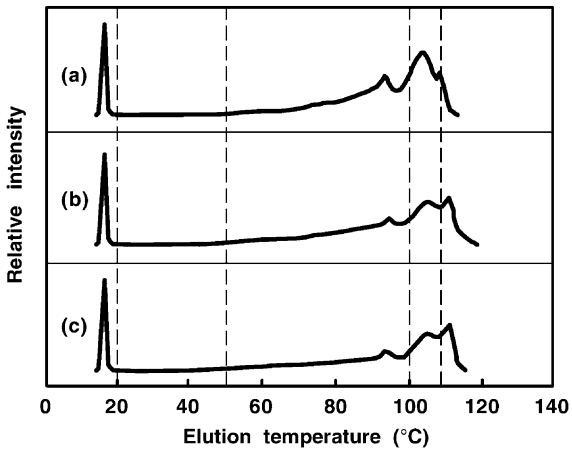
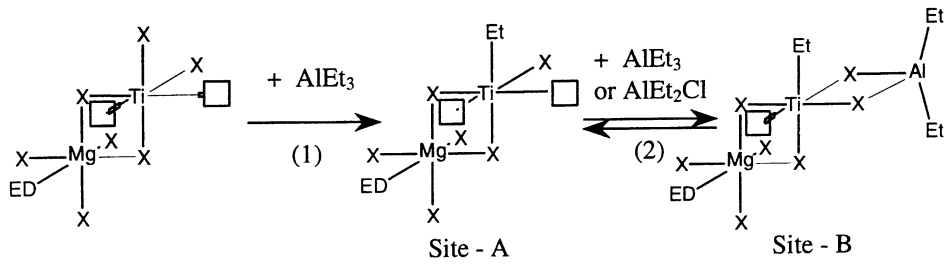


Fig. 4. Dependence of TREF profiles on catalyst pretreatment time for polypropenes obtained in stopped-flow polymerization with the TEA-pretreated $TiCl_4$/DBP/$Mg(OEt)_2$ catalysts. TEA pretreatment time: (a) 10 s; (b) 60 s; (c) 600 s.

procedure. These unique features of this catalyst in terms of slow active sites formation, and slow deactivation upon TEA pretreatment may be mainly ascribed to its raw material, that is the effect of $–OC_2H_5$ ligand, which can decrease the reduction potential of the original surface tetravalent titanium species as well as the reduction potential of the active titanium species due to its electron donation property. This may be one of the main reasons that account for the existence of an induction period (∼0.2 s) and the high stability of the active sites on this catalyst. The effect of the catalyst preparation method may not be completely ruled out. The cocatalyst pretreatment-dependent gradually increase in activity of the $Mg(OEt)_2$-supported Ziegler–Natta catalyst system has also been observed in our previous study [5]. Table 1 also shows the weight fractions of polypropenes obtained by TREF method. Each PP sample is fractionated in four different temperature ranges, namely ∼20, 20–100, 100–110 and 110–140 °C, which are thought to be corresponding to four kinds of active sites with different isospecificity defined as aspecific active site (AS site, creating the ∼20 °C fraction), semi-isospecific active site (IS_1 site, producing the 20–100 °C fraction), the second highest isospecific active site (IS_2 site, making the 100–110 °C fraction) and the highest isospecific active site (IS_3 site, generating the 110–140 °C fraction), respectively. It can be seen from Table 1 that there exist four kinds of active sites on the catalyst with 2 s of TEA pretreatment reflecting a broad multiplicity in the isospecificity of active sites: AS, IS_1, IS_2 and IS_3 sites, which are corresponding to a strong sharp peak at below 20 °C, a weak and broad area between 20 and 100 °C with a peak at ca. 95 °C, a strong peak at ca. 104–105 °C, and a weak peak at ca. 110 °C in TREF curve (a) of Fig. 4, respectively. In comparison with $MgCl_2$-supported Ziegler–Natta catalysts [38], a newly emerged peak at ca. 95 °C for all the TREF curves is an indication of the presence of a new type of active surface titanium species (here defined as the third highest isospecific active sites expressed as IS_1^* site, which are included in the IS_1 site) and more dispersed state of isospecificity of active sites on $Mg(OEt)_2$-supported Ziegler–Natta catalysts. The multiplicity of active sites for $Mg(OEt)_2$-supported catalysts has also been reported in [45,46]. Taking the ligand effect into consideration, these IS_1^* site might be related to the $–OC_2H_5$ ligand. As illustrated by Lee et al. [47], the presence of the $–OC_2H_5$ ligand made the reactions in the catalyst preparation much more complicated. As shown in Table 1, the successive and significant increasing of the 110–140 °C PP fraction (over 100% increasing of 110–140 °C PP

fraction from 10 to 60 s of pretreatment, while the corresponding decrease of overall active site concentration from 10 to 60 s is only ca. 30% as shown in Fig. 3) with increasing length of TEA pretreatment time up to 60 s indicates the successive time-delayed formation of the highest isospecific active sites (IS_3 site) from 10 to 60 s of pretreatment time, which also can be seen from the obvious increase of intensity of the TREF curve peak at 110–140 °C, as well as the peak shifting towards higher elution temperature, from TREF curves (a) and (b) in Fig. 4. This fact also coincides with the successive and significant increasing of chain propagation rate constant and number average molecular weight up to 60 s of TEA pretreatment as shown in Table 1. As it is generally accepted that the chain propagation rate constant of different types of active sites significantly increases with augment of isospecificity of the active sites [30,48]. Here it is a clear demonstration that there exists a successive time-delayed formation of active sites with the highest isospecificity (IS_3 site) under the TEA pretreatment procedure (up to 60 s of pretreatment), so to speak the formation of active sites with the highest isospecificity (IS_3 site) still strongly depends on the interaction between the catalyst and the Al-alkyl cocatalyst (up to 60 s of pretreatment) even in the presence of internal electron donor DBP in this catalyst. There are two reasons that may account for this phenomenon. The first possible explanation is that the activation (reduction and alkylation) of the precursors of active sites with the highest isospecificity is the slowest due to the corresponding highest steric hindrance around and thus results in the slowest formation of IS_3 site in the early stage of the pretreatment procedure (up to 60 s of pretreatment). Whereas, it is evident from Table 1 that some active sites with the highest isospecificity were formed in the much earlier stage of TEA pretreatment (10 s of pretreatment). The first mechanism cannot explain this time-delayed formation characteristics well and thus is unreasonable. While the second possible mechanism might be that some active sites with lower isospecificity (AS, IS_1 or IS_2 site), which were formed after the first activation (reduction and alkylation) process, were transformed into active sites with the highest isospecificity (IS_3 site) through some secondary reactions between the activated titanium species and the cocatalyst, e.g. TEA (or the by-products of the first reduction and alkylation process, e.g. DEAC) in the early stage of the TEA pretreatment procedure (up to 60 s of pretreatment). These secondary reactions should be the reversible bimetallic complexing reactions between the catalyst and the cocatalyst, e.g. TEA (or the by-products of the first reduction and alkylation process, e.g. DEAC). Such reversible bimetallic complexing reactions have been previously suggested by some researchers for explaining the presence of stereoblock microstructures in polypropenes produced by supported Ziegler–Natta catalysts [11–13]. Monometallic active sites are thought to be aspecific or less isospecific, while bimetallic active sites are envisioned to be highly isospecific. In this work, our experimental evidence might directly demonstrate the dynamic process of transformation of active sites with lower isospecificity into the highest isospecific active sites through interaction between the catalyst and cocatalyst up to 60 s of pretreatment in approaching to an equilibrium sate of monometallic and bimetallic active sites as proposed by Xu et al. [12]. The results somewhat suggest that the contribution from the bimetallic active sites to the stereospecificity of the Ziegler–Natta catalysts cannot be overlooked even in the presence of internal electron donor through a plausible mechanism as shown in Scheme 1. After the first step of instant alkylation (reaction (1)), an aspecific active site (site A) might be obtained. Further TEA pretreatment might induce the bimetallic complexing (reaction (2)) leading to the formation of site B. According to a generalized stereospecific active site model proposed by Busico and coworkers [13,49] recently, site B is a kind of highly isospecific active site. This mechanism seems highly possible and feasible in explaining the time-delayed successive formation of active sites with the highest isospecificity.

The formation of the other three types of active sites with lower isospecificity (i.e. AS, IS_1 and IS_2 sites) seems already finished up to 10 s of TEA pretreatment in the presence of internal electron donor judging from the data shown in Table 1 and Fig. 4. The obvious deactivation of active sites, which occurred from 10 to 60 s of TEA pretreatment, is mainly due to the deactivation of AS, IS_1 and IS_2 sites. The stability of active sites increases with the increasing isospecificity of the active sites in the early stage of TEA pretreatment (up to 60 s of pretreatment). This might be rationalized by the facts that the active sites with



Scheme 1. Plausible mechanism of transformation of aspecific active site into highly isospecific active site in the presence of internal electron donor (ED) (X: –Cl or –Et or –OEt; □: coordination vacancy).

higher isospecificity are usually less acidic as well as less accessible (due to higher steric hindrance) and thus more over-reduction resistant to TEA pretreatment [15]. Thereafter, all types of active sites on the catalyst become relatively stable in the later stage of TEA pretreatment from 60 to 600 s of pretreatment, which also accounts for the high stability in activity, number average molecular weight and chain propagation rate constant in this period of TEA pretreatment. This indicates that the residual active sites regardless of isospecificity are relatively more stable after deactivation of the unstable part of each type of active site. The extraction of internal electron donor DBP by the TEA from the isospecific active sites on the catalyst in the TEA pretreatment procedure is thought to have occurred from 60 s of pretreatment judging from the slight decrease in relative weight percentages of the 110–140, 100–110 and 20–100 °C PP fractions as well as simultaneous obvious increase in relative weight percentage of the ∼20 °C PP fraction in the later stage of TEA pretreatment (from 60 to 600 s of pretreatment, see Table 1 and the tendency from TREF curves (b) and (c) in Fig. 4). This is an indication of slight transformation of isospecific active sites into aspecific sites due to extraction of internal donor DBP by TEA resulted from longer period of TEA pretreatment (from 60 to 600 s of pretreatment). This reflects the dynamic process of interaction between cocatalyst and internal donor approaching to an equilibrium sate as suggested by Sacchi et al. [11] to explain the formation of stereoblock microstructures in polypropenes produced by supported Ziegler–Natta catalysts in the presence of electron donor. In this work, our experimental evidence might directly visualize the dynamic process of the initiation of electron donor extraction from the catalyst surface by TEA cocatalyst from 60 up to 600 s of pretreatment in approaching to the equilibrium sate. The DBP extraction extent by TEA was observed to be much lower than the case when ethylbenzoate (EB) was used as internal donor [38]. This is consistent with some previous reports that DBP as internal donor can coordinated much more strongly with the catalyst surface and thus is much more difficult to be extracted by the TEA cocatalyst during the polymerization process compared with EB [15,22,38]. The high retention ability of the internal donor DBP in this catalyst responded to the extraction behavior from TEA cocatalyst may also partially contribute to the relatively high stability of active sites due to DBP's steric and electronic effects.

In this work, the new concept of model reactions in terms of stopped-flow propene polymerizations using supported Ziegler–Natta catalysts under a TEA cocatalyst pretreatment procedure with varied length of pretreatment time from 0 to 600 s combined with GPC and TREF methods have been demonstrated to be most efficient in probing the mechanism concerning the dynamic successive formation, deactivation and transformation of stereospecific active sites on supported Ziegler–Natta catalysts during a conventional polymerization process. Many valuable new evidences concerning the formation, deactivation and transformation mechanisms as well as the stereochemical nature of the active sites had been obtained with respect to the roles of Al-alkyl cocatalyst, electron donor, catalytic component, etc. Several attempts using other highly efficient supported Ziegler–Natta catalysts under Al-alkyl cocatalyst pretreatment procedure accomplished by the combination of stopped-flow technique with TREF method and GPC analyses will

also be available for publication, in which more profound insights into the stereochemical nature of active sites will surely be achieved progressively. The objective is to pursue a state-of-the-art catalyst designing for developing novel tailor-made polyolefins with ultimate stereospecificity.

4. Conclusions

The difficulties in pursuing basic understanding on the formation mechanism and stereochemical nature of active sites as well as the stereospecific polymerization mechanism in heterogeneous Ziegler–Natta catalysis was partially overcome by utilizing the great merits of stopped-flow technique combined with TREF and GPC methods. Furthermore, a TEA cocatalyst pretreatment procedure (from 0 to 600 s of pretreatment time) provided direct observation of the dynamic process of formation, deactivation and transformation of stereospecific active sites on a $TiCl_4$/DBP/$Mg(OEt)_2$ catalyst. It was demonstrated that both formation and deactivation of active sites with broad multiplicity in isospecificity (reflected from the coexistence of four kinds of stereospecific active sites, namely AS, IS_1, IS_2 and IS_3 sites for all the pretreated catalysts) are slow reactions with an induction period of ca. 0.2 s. It was most important to find that the formation of active sites with the highest isospecificity (IS_3 site) still strongly depends on the interaction between the catalyst and cocatalyst (up to 60 s of pretreatment) even in the presence of internal electron donor DBP. This is proposed to originate from a secondary reversible bimetallic complexing reaction between the catalyst and the cocatalyst (or its reaction products) in the early stage of TEA pretreatment procedure (up to 60 s of pretreatment) resulting in the time-delayed successive formation of some bimetallic active sites with the highest isospecificity (IS_3 site). The existence of $–OC_2H_5$ ligand most probably gave birth to a new group of active titanium species (IS_1^* site included in IS_1 site). The stability of active sites increases with increasing isospecificity in the early stage of pretreatment (up to 60 s of pretreatment). While all the active sites become relatively stable in the later stage of pretreatment (from 60 to 600 s of pretreatment). The extraction of internal electron donor DBP by the TEA from the catalyst surface within the TEA pretreatment procedure is thought to have occurred from 60 s of pretreatment resulting in slight transformation of isospecific active sites into aspecific sites.

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References

[1] J.J.A. Dusseault, C.C. Hsu, J. Macromol. Sci., Rev. Macromol. Chem. Phys. C33 (1993) 103.
[2] P.C. Barbé, G. Cecchin, L. Noristi, Adv. Polym. Sci. 81 (1987) 1.
[3] H. Mori, M. Yoshitome, M. Terano, Macromol. Chem. Phys. 198 (1997) 3207.
[4] M. Kakugo, H. Sadatoshi, J. Sakai, in: T. Keii, K. Soga (Eds.), Catalytic Olefin Polymerization, Kodansha/Elsevier, Tokyo, 1990, p. 345.
[5] H. Mori, M. Yamahiro, M. Terano, M. Takahashi, T. Matsukawa, Macromol. Chem. Phys. 201 (2000) 289.
[6] N. Kashiwa, J. Yoshitake, Makromol. Chem. 185 (1984) 1133.
[7] V. Busico, P. Corradini, A. Ferraro, A. Proto, Makromol. Chem. 187 (1986) 1125.
[8] J.C.W. Chien, J.C. Wu, J. Polym. Sci., Part A: Polym. Chem. 20 (1982) 2461.
[9] S. Weber, J.C.W. Chien, Y. Hu, J. Polym. Sci., Part A: Polym. Chem. 27 (1989) 1499.
[10] B. Liu, H. Matsuoka, M. Terano, Macromol. Rapid Commun. 22 (2001) 1.
[11] M.C. Sacchi, L. Tritto, P. Locatelli, Prog. Polym. Sci. 16 (1991) 331.
[12] J. Xu, L. Feng, S. Yang, Macromolecules 30 (1997) 2539.
[13] V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, Macromolecules 32 (1999) 4173.
[14] M. Yamahiro, H. Mori, K. Nitta, M. Terano, Macromol. Chem. Phys. 200 (1999) 134.
[15] V. Busico, P. Corradini, L.D. Martino, A. Proto, V. Savino, Makromol. Chem. 186 (1985) 1279.
[16] N. Kashiwa, J. Yoshitake, A. Toyota, Polym. Bull. 19 (1988) 333.
[17] V. Busico, P. Corradini, L.D. Martino, A. Proto, Makromol. Chem. 187 (1986) 1115.
[18] L. Noristi, P.C. Barbè, G. Baruzzi, Makromol. Chem. 192 (1991) 1115.
[19] C.B. Yang, C.C. Hsu, Macromol. Rapid Commun. 16 (1995) 311.
[20] M.C. Sacchi, I. Tritto, C. Shan, R. Mendichi, L. Noristi, Macromolecules 24 (1991) 6823.

[21] M.C. Sacchi, F. Forlini, I. Tritto, R. Mendichi, G. Zannoni, L. Noristi, Macromolecules 25 (1992) 5914.
[22] K. Soga, T. Shiono, Y. Doi, Makromol. Chem. 189 (1988) 1531.
[23] H. Mori, M. Terano, Trends Polym. Sci. 5 (1997) 314.
[24] H. Mori, H. Saito, M. Terano, Macromol. Chem. Phys. 199 (1998) 55.
[25] H. Mori, H. Saito, M. Yamahiro, H. Kono, M. Terano, Macromol. Chem. Phys. 199 (1998) 613.
[26] H. Mori, H. Yamada, H. Kono, M. Terano, J. Mol. Catal. A: Chem. 125 (1997) L81.
[27] H. Mori, M. Endou, K. Tashino, M. Terano, J. Mol. Catal. A: Chem. 145 (1999) 153.
[28] H. Mori, K. Tashino, M. Terano, Macromol. Rapid Commun. 16 (1995) 651.
[29] H. Mori, M. Yamahiro, K. Tashino, K. Ohnishi, K. Nitta, M. Terano, Macromol. Rapid Commun. 16 (1995) 247.
[30] H. Matsuoka, B. Liu, H. Nakatani, M. Terano, Macromol. Rapid Commun. 22 (2001) 326.
[31] H. Mori, H. Kono, M. Terano, Macromol. Chem. Phys. 201 (2000) 543.
[32] H. Mori, M. Yamahiro, M. Terano, M. Takahashi, T. Matsukawa, Die Angewandte Makromolekulare Chemie 273 (1999) 40.
[33] H. Mori, M. Yamahiro, V.V. Prokhorov, K. Nitta, M. Terano, Macromolecules 32 (1999) 6008.
[34] H. Mori, K. Hasebe, M. Terano, J. Mol. Catal. A: Chem. 140 (1999) 165.
[35] M. Yamahiro, H. Mori, K. Nitta, M. Terano, Polymer 40 (1999) 5265.
[36] H. Mori, H. Iguchi, K. Hasebe, M. Terano, Macromol. Chem. Phys. 198 (1997) 1249.
[37] H. Mori, M. Endou, M. Terano, J. Mol. Catal. A: Chem. 145 (1999) 211.
[38] B. Liu, T. Nitta, H. Nakatani, M. Terano, in preparation.
[39] M. Kakugo, T. Miyatake, Y. Naito, K. Mizunuma, Macromolecules 21 (1988) 314.
[40] M. Kakugo, T. Miyatake, Y. Naito, K. Mizunuma, Makromol. Chem. 190 (1989) 505.
[41] G. Morini, E. Albizzati, G. Balbontin, I. Mingozzi, M.C. Sacchi, F. Forlini, I. Tritto, Macromolecules 29 (1996) 5770.
[42] J. Xu, Y. Yang, L. Feng, X. Kong, S. Yang, J. Appl. Polym. Sci. 62 (1996) 727.
[43] J. Xu, L. Feng, S. Yang, Y. Yang, X. Kong, Polym. J. 29 (1997) 713.
[44] M. Kioka, H. Makio, A. Mizuno, N. Kashiwa, Polymer 35 (1994) 580.
[45] L.L. Bohm, Polymer 19 (1978) 562.
[46] K.H. Reichert, in: Proceedings of the 28th IUPAC Macromolecules Symposium Amherst, Mass., 12–16 July 1982, p. 255.
[47] D.H. Lee, Y.T. Jeong, K.K. Kang, Stud. Surf. Sci. Catal. 89 (1994) 135.
[48] K. Soga, M. Ohgizawa, T. Shiono, Makromol. Chem. Rapid Commun. 10 (1989) 503.
[49] V. Busico, R. Cipullo, Prog. Polym. Sci. 26 (2001) 443.