Microstructure of isotactic polypropylene obtained using Ziegler–Natta catalyst at high polymerization temperature

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ABSTRACT: The microstructure of the isotactic polypropylene obtained with various $MgCl_2$-supported catalyst systems at high polymerization temperature of 70–100°C is investigated by discussing the intrinsic relation between the different types of active centers and the polymerization temperatures via gel permeation chromatography, temperature rising elution fractionation, and ^{13}C NMR. For the $MgCl_2/TiCl_4/$di-n-butyl phathalate-$AlEt_3$/external donor and $MgCl_2/TiCl_4/$2,2-diisobutyl-1,3-dimethoxypropane-$AlEt_3$ catalyst systems, the differences in the isotactic productivity of polymers obtained at different polymerization temperatures mainly result from the variation of both the activity of the different isospecific active centers and the stability constants of the complex of catalyst/donor. The reaction rate of high isotactic active centers reaches maximum at 85–90°C, and this effect contributes to both the highest isotacticity and the narrowest molecular weight distribution. For the $MgCl_2/TiCl_4/$phthalate ester-$AlEt_3$ catalyst system, the isotacticity of polypropylene remains approximately constant in the temperature range of experiments, which could be ascribed to elution of phthalate ester after the activation. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42487.

INTRODUCTION

It is well known that different polymerization conditions can result polypropylenes with different microstructures and final application properties.[1–8] Over the years, basic studies have aimed at revealing the inherent relations between the polymerization conditions and the microstructures of isotactic polypropylene.[6–10] Polymerization temperature plays a critical role in propylene polymerization process with different Ziegler–Natta catalyst systems for modifying the microstructure of polypropylene.[11–13] The effects of polymerization temperature on the relative chemical structures of isotactic polypropylene with different Ziegler–Natta catalyst systems were reported. Rishina *et al.*[14] showed that for a $TiCl_3$-$AlEt_3$ catalyst system, the stereoregularity of the isotactic polymer fraction decreased with the increment of polymerization temperature from −25 to 30°C, while that increased with the polymerization temperature increasing from 30 to 120°C. Zhong *et al.*[15] reported that for the $MgCl_2/TiCl_4$-$AlEt_3$ catalyst system, the stereoregularity of isotactic polymer fraction remained approximately constant when the polymerization temperature was in the range of 70–120°C. For the $MgCl_2/TiCl_4/$phthalate ester-$AlEt_3$ catalyst system, when the polymerization temperature was raised from 40 to 80°C, no

increment in the stereoregularity of isotactic polymer fraction was observed without external donor.[12] However, if the external donor was added, the stereoregularity of isotactic polymer fraction turned to increase with temperature rising. Meanwhile, Chadwick[12] also found that for the $MgCl_2/TiCl_4/$diether-$AlEt_3$ catalyst system, even though the polymerization was in the absence of external donor, the polymerization temperature increasing from 40 to 80°C led to the significant increase in the stereoregularity of isotactic polymer fraction.

In general terms, the industrial polymerization temperature is around 70–80°C for $MgCl_2$-supported Ziegler–Natta catalyst systems. However, the higher polymerization temperature (>80°C) is preferred in industries to reduce the burden of removing the polymerization heat in commercial plants.[11,16] It is well known that the activity of catalyst decreases if the polymerization temperature is over 80°C using $MgCl_2$-supported Ziegler–Natta catalyst systems in propylene polymerization. Moreover, the effect of polymerization temperature on the microstructure of polypropylene is ambiguous with different catalyst systems at higher polymerization temperatures. Therefore, these would limit to apply the polypropylene polymerization with higher polymerization temperature. Many efforts have

been devoted to investigate the mechanisms of the influence of polymerization temperature on the polypropylene microstructure, and those explanations predominantly focused on the polymerization temperatures below 80°C.

In this article, the polymerizations were carried out with various MgCl₂-supported catalyst systems in the polymerization temperature range from 70 to 100°C with or without hydrogen. Although a single type of active centers mode simplifies the way to understand the behavior of catalyst systems, it has been demonstrated that there exists no simple way to separate the different types of active centers at the catalyst surface by various chemical or thermal modifications and thus to approach a single type of active centers model from multi-types of actives centers.[5,17,18] From this observed collective behavior, we aimed to discuss the intrinsic relationship between the different types of active centers and the polymerization temperatures through the analysis of gel permeation chromatography (GPC) date of polypropylene samples obtained at different polymerization temperatures, the distributional stereoregularity of polypropylene from analysis of temperature rising elution fractionation (TREF) data, and the ^{13}C NMR data of corresponding samples.

EXPERIMENTAL

Preparation of Catalyst

The MgCl₂/TiCl₄/internal donor catalysts were prepared by reaction of a spherical adduct MgCl₂·nEtOH with TiCl₄ in the presence of di-n-butyl phthalate (DNBP) or 2,2-diisobutyl-1,3-dimethoxypropane (DIBDMP) as the internal donor, using procedures similar to that described in the CN patent 103,788,237. The content of titanium in MgCl₂/TiCl₄/DNBP catalyst and MgCl₂/TiCl₄/DIBDMP were 2.16 and 2.32 wt %, respectively.

Polymerization

All polymerization reactions were carried out in 1800 mL of liquid propylene at target polymerization temperature in a 3.3-L reactor with triethylaluminum (AlEt₃) as the cocatalyst and cyclohexyl methyl dimethoxy silane (CHMDMS) or dicyclopentyl dimethoxy silane (DCPDMS) as the external donor. Typically, the target amount of hydrogen was added into the reactor. The molar ratio of AlEt₃ to Ti (Al/Ti) was 300, and the molar ratio of external donor to Ti was 15. The polymerization time was 1 h and the polymerization was stopped with the addition of 0.5 mL of isopropanol in 2.5 mL of pentane.

Characterization

Titanium content of the catalyst was measured on a 722 spectrophotometer.

Isotactic index (I.I.) of sample was measured by extracting the samples for 8 h with boiling n-heptane in a Soxhlet-type apparatus. The weight percent of the heptanes-insoluble fraction in a whole sample is referred to as the *isotactic index*.

^{13}C-NMR spectra of PPs were recorded with a Bruker AVANCE||| 400 MHz spectrometer (Bruker Instruments, Billerica, MA) operating at 100.6 MHz, on 10–20 mg/mL solutions in deuterated dichlorobenzene at 110°C (conditions: 5 mm probe; pulse repetition 4 s; numbers of scans 20,000).

GPC was carried out at 140°C using Waters Alliance GPCV 2000 (Waters, Milford, Massachusetts). The mobile phase was 1,2,4-tri-

Table I. Effects of the Polymerization Temperature on the Polymerization of Propylene Using MgCl₂/TiCl₄/DNBP-AlEt₃/CHMDMS Catalyst System with a 0.3 mol % Hydrogen Concentration

$T_{pol.}$	Activity	M_w	MWD	I.I.[a]	mmmm[b]
°C	kgPP/gcat h	×10³		wt %	%
70	50.2	256	6.14	97.2	92.9
80	55.5	240	5.26	97.8	93.4
85	60.7	209	4.65	98.5	94.0
90	43.8	173	4.81	98.1	93.7
100	25.6	151	5.03	97.7	93.3

[a] Isotactic index: weight percent of heptane-insoluble fraction.
[b] Calculated by ^{13}C NMR.

chlorobenzene and the flow rate of 1 mL/min was used. An injection volume of 220 μL was used at 0.5mg/mL. To prevent degradation, 0.1 mg/mL of the stabilizer BHT was used.

TREF measurement was carried out by dissolving 1 g of the polymer sample in 1,2,4-trichlorobenzene at 160°C and is maintained for 60 min. To prevent degradation, 0.1 mg/mL of the stabilizer BHT was used, and then cooled to 100°C at a cooling rate of 8°C/min, and further cooled to 25°C at a cooling rate of 4°C/min and maintained for 60 min. Thereafter, o-dichlorobenzene (including 0.5 mg/mL of BHT) as a solvent was flowed through the column at 25°C at a flow rate of 1 mL/min, so that a component dissolved in o-dichlorobenzene at −15°C in the TREF column was eluted for 10 min, and then the column was heated linearly at a heating rate of 100°C/h to 140°C to obtain an elution curve.

Differential scanning calorimetry (DSC) measurement was carried out on the Perkin Elmer series 7 TA System. The sample was precrystallized by melting them at 220°C followed by cooling at a rate of 20°C/min to 25°C. The measurements were carried out in the range of 30–180°C at a rate of 5°C/min.

Successive self-nucleation and annealing (SSA) fractionation was performed by the previous literatures.[19,20] The sample was melted at 200°C for 5 min, then it was cooled at 20°C/min to 30°C in order to erase the crystalline thermal history. Subsequently, a heating scan at 20°C/min was performed up to a selected self-seeding and annealing temperature denoted T_s. The sample was kept at T_s for 15 min before cooling it again at 20°C/min down to 30°C. Then the sample was repeated last step at increasingly lower T_s, which was lowered at 5°C intervals with respect to the previous step. The chosen T_s range was 169 to 139°C. Finally, the sample was heated at 10°C/min from 30 to 200°C, and a multiple melting endotherm was obtained.

RESULTS AND DISCUSSION

At first, the polymerization of the propylene was carried out at the polymerization temperature of 70 to 100°C using MgCl₂/TiCl₄/di-n-butyl phthalate (DNBP)-AlEt₃/cyclohexyl methyl dimethoxy silane (CHMDMS) catalyst system with of the hydrogen concentration of 0.3 mol %, and the results are shown in Table I. It can be seen that the average activity in the polymerization gradually increased from 50.2 to 60.7 KgPP/gcat h
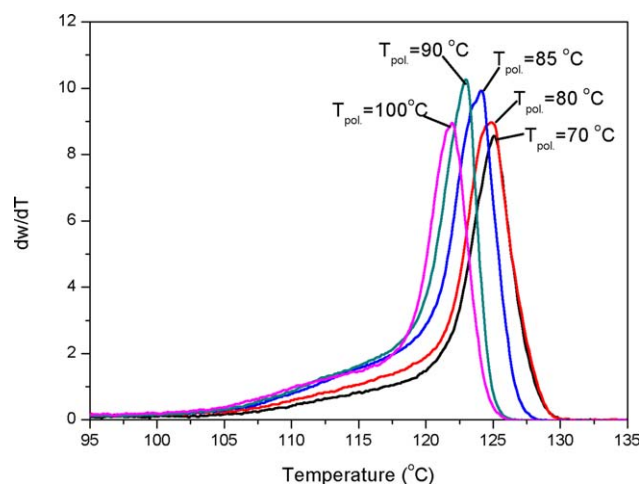
Figure 1. TREF elution profiles of polypropylene prepared at various polymerization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when the polymerization temperature increased from 70 to 85°C. However, a significant decrease in the average activity is observed at still higher polymerization temperature. As shown in Table I, the average activity decreases to about 25.6 kgPP/gcat h when the polymerization temperature increases from 85 to 100°C. Furthermore, both average isotactic index (I.I) and the average mmmm pentad content of the polypropylene product gradually increase at the temperature range from 70 to 85°C, while they slightly decrease when the temperature further increases to 100°C. Note that in this article, the precision of both average isotactic index value and average mmmm pentad content value was ±0.1 for the same polypropylene sample.

^{13}C NMR measurements provide the average isotacticity of polypropylene. It describes the nature of occasional steric defects in isotactic chains.[21,22] However, the information derived from ^{13}C NMR data is insufficient to understand the potential mechanism of propylene polymerization reaction. TREF data presents various stereo-defects in the high isotacticity faction, and the stereo-defects are not necessarily present in the same macromolecules. Therefore, the TREF elution profiles of the polypropylene are considered essential as their tacticity profiles.[13] In order to better characterize the polymers, a TREF analysis was carried out in the temperature range from 25 to 140°C. Figure 1 shows the TREF elution profiles of polypropylene samples prepared at various polymerization temperatures. All the samples obtained by the series of experiments have a similar tacticity distribution, while the main elution peak slightly shifts toward low temperature with the polymerization temperature increasing from 70 to 100°C. Morini *et al.* had measured the intrinsic viscosity of the fractions, which were obtained by the TREF analysis of the polypropylene product, and they found that the intrinsic viscosities of the fractions increased with the elution temperature increasing, and then the sequence length increased almost linearly with the elution temperature.[23,24] Moreover, from the data in Table I, it is found that the average molecular weights decrease with the polymerization temperatures increasing, and thus, the main peaks of

TREF elution curves decrease as the polymerization temperature increasing. However, the peak intensity of the product obtained at the polymerization temperature of 85°C is stronger than that of other products. In order to facilitate the presentation of the results of TREF, the elution fractions of polypropylene is subdivided into four regions, and the weight fraction eluted at each region is calculated as shown in Table II. As already observed by Morini,[23] the higher the elution temperature ($T_{el.}$) of the region, the higher the isotacticity of the corresponding fractionation. It can be seen from Table II that, compared with other regions, region D locates at the highest $T_{el.}$ and thus corresponds to the fraction with relative highest isotacticity; on the other hand, region C and region B located at lower $T_{el.}$ and correspond to relative medium and low isotacticity; meanwhile, region A locates at the lowest $T_{el.}$, which is a soluble fraction at room temperature, and thus corresponds to the atactic fraction. It is observed that the content of each fraction remains approximately the same degree, independently of polymerization temperature. The fraction of region D reaches a maximum at the polymerization temperature of 85°C, and then decreases moderately. However, a moderate increase in the fraction of region C with the polymerization temperature increasing is apparent. The fractions of region A and region B significantly increase when the polymerization temperature increases from 70 to 85°C, while the fractions of region A and region B decrease with further increasing the polymerization temperature to 100°C. It is demonstrated that the low isotactic active centers are not preferentially deactivated at the elevated polymerization temperature.

Figure 2 shows all GPC curves of the polypropylene samples produced by different polymerization temperatures corresponding to conditions of Table I. It is well known that polymers produced with solid Ziegler–Natta catalyst systems have broad molecular weight distributions (MWD) because of multi-types of active centers in these catalyst systems. Those different types active centers are commonly called Flory components.[13] During the polymerization reactions, each type active center is characterized by the same ratios of chain transfer rate constant and the chain propagation rate constant. As a result, molecular weight distribution of each type active center corresponds to MWD = 2.0.[25,26] As shown in Figure 2, the polypropylene samples obtained at the different polymerization temperatures exhibit a pronounced change in the GPC curves shape, whereas the end points of the GPC curves remain at approximately the

Table II. Content Distribution of Soluble Fractionation of Samples at Different Elution Temperature Regions on the TREF Curves (The Samples were Prepared at Different Polymerization Temperature)

$T_{pol.}$ (°C)	70	80	85	90	100
(A) $T_{el} < 25$°C (wt %)	2.15	1.26	1.08	1.24	1.82
(B) $T_{el} = 25$–99°C (wt %)	10.24	8.58	7.85	9.46	12.47
(C) $T_{el} = 99$–110°C (wt %)	3.02	3.25	3.74	4.30	5.60
(D) $T_{el} = 110$–135°C (wt %)	84.59	86.91	87.33	85.00	80.11
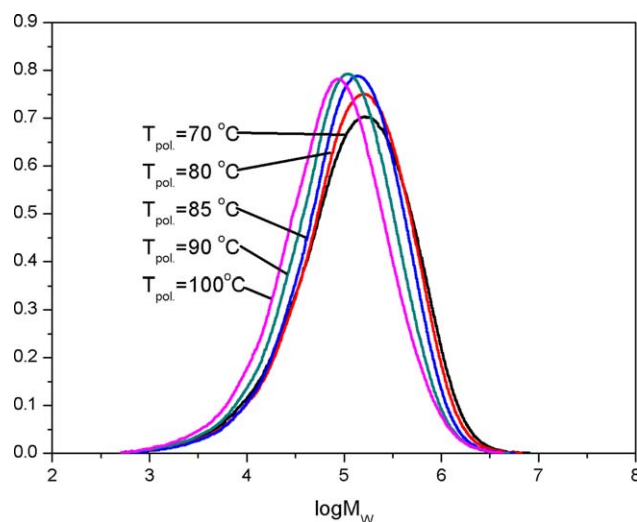
Figure 2. GPC curves of the polypropylenes produced at different polymerization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

same molecular weights. It is indicated that there exist not any type of active center, which are in the catalyst system of this series experiments, can unlikely be deactivated by changing the polymerization temperature. Chadwick also found the same result that the poor isotacticity active centers are not preferentially deactivated at elevated polymerization temperature.[12]

DSC analysis is especially sensitive to the thermal properties of polymer components with the highest crystallinity due to the highest isotacticity.[13,20] Figure 3 shows the DSC melting curves of the polypropylene samples obtained at different polymerization temperatures. As shown in Table I, the average isotacticity degree of samples, which were obtained by different polymerization temperature, is similar. It can be predicted that the fraction of highest isotacticity of those samples is also similar. Therefore, it is not easy to distinguish the maximum peak position of the DSC melting curves of the samples from Figure 3. According to the curves of Figure 3, each polymer has at least two components of different high isotacticity and the peaks of those components have some obvious overlap.

Successive self-nucleation and annealing (SSA) fractionation is widely used in the characterization of the microstructure of polypropylene.[20,27] It is because that the SSA fractionation can promote the potential molecular fractionation occurred during crystallization by applied self-nucleation and annealing steps sequentially. Differences in isotacticity of polypropylene can be magnified by the SSA fractionation.[20] On the other hand, the SSA fractionation is not sensitive to molecular weight and distribution of polymer.[19]
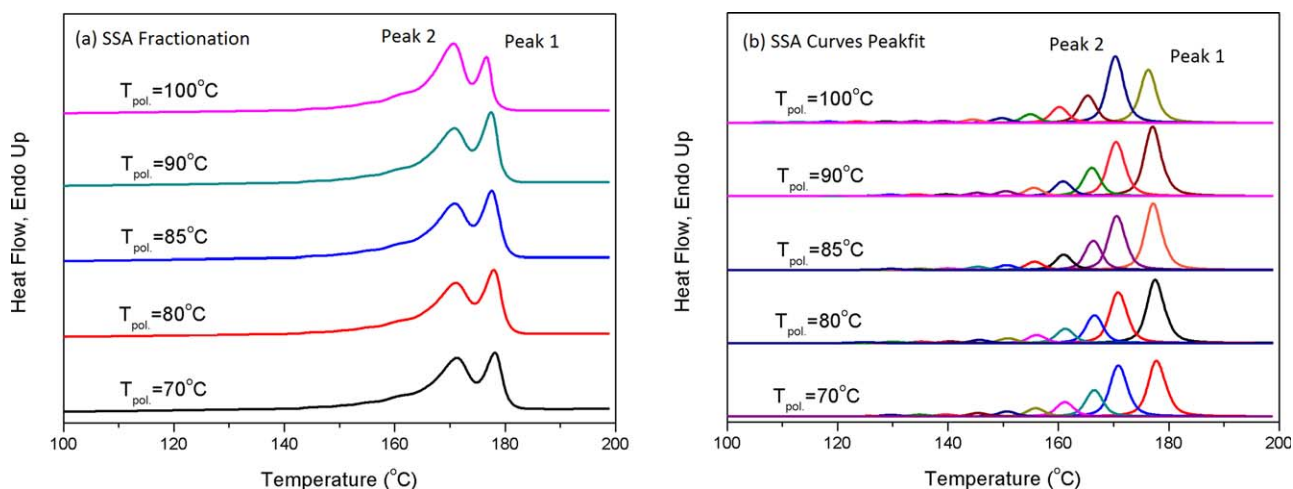
Figure 4(a) shows the SSA final melting curves of samples, which were obtained by different polymerization temperature. The SSA curves are fitted using Peakfit 4.12, as shown in Figure 4(b). The SSA curves comprise two main peaks on the high temperature and several minor peaks on the low temperature region. In this article, the main peaks of the SSA-fitted curves located at the highest temperature region is denoted as Peak 1;

another main peak is Peak 2, which is located at higher temperature region. The higher the melting temperature, the higher the isotacticity of the fractionation.[20,27] As shown in Figure 4, the Peak 1, therefore, corresponds to the fraction with relative highest isotacticity. Figure 5 shows the melting temperature (T_m) of Peak 1 and Peak 2 for the SSA curves of the samples obtained by different polymerization temperature. As seen in Figure 5, the T_m of Peak 1 and Peak 2 for the SSA final melting curves of samples, which were produced at different polymerization temperature, decrease with the increasing of the polymerization temperature. This is in agreement with $T_{el.}$ of samples, as shown in Figure 1. The results clearly indicate that the isotacticity of highest isotactic fractionation of those sample decrease with the increasing of polymerization temperature. In order to quantitatively evaluate the variation of each melting peak of those SSA-fitted curves, the relative contents of Peak 1 and Peak 1 + Peak 2, which are the integral area percentages on the SSA-fitted curves, are shown in Figure 6. The relative contents of Peak 1 reach a maximum at the polymerization temperature range of 85–90°C, and then decreased moderately; meanwhile, the relative contents of Peak 1 + Peak 2 increase when the polymerization temperature increases from 70 to 85°C, while it decreases with further increasing the temperature to 100°C. This is in agreement with the contents distribution of soluble fractionation of samples at different elution temperature regions on the TREF curves. The relative content of region D reaches the maximum value at 85°C, as shown in Table II. It is clearly indicated that with increase of polymerization temperature from 70 to 85°C, the amount of the active centers of highest isotacticity increases gradually, and then it decreases gradually above 85°C. Therefore, both average isotactic index and the average mmmm pentad content of the polypropylene product gradually increase at the temperature range from 70 to 85°C, while they slightly decrease when the temperature further increases to 100°C, as shown in Table I.

In order to evaluate the effect of adding hydrogen on the average isotatic index of polymers, a series of polymerizations were
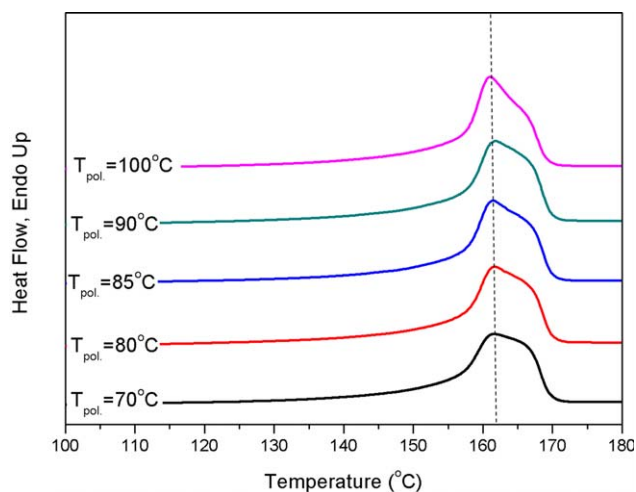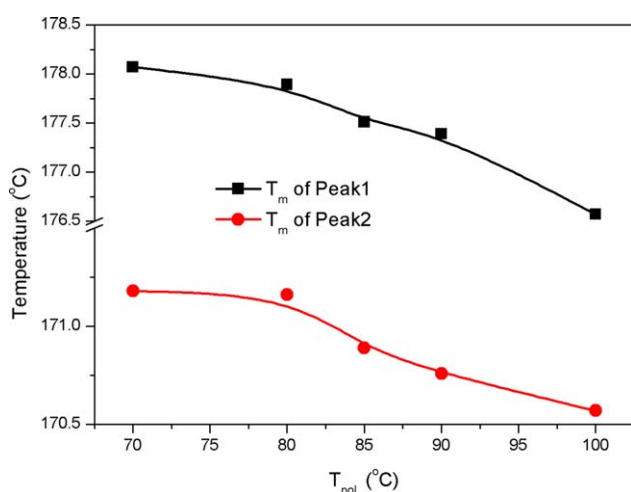

Figure 3. DSC melting curves of the polypropylene samples obtained at different polymerization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. (a) SSA final melting curves of samples obtained by different polymerization temperature. (b) Fitted curves using Peakfit 4.12 software of the SSA final melting curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also carried out in the absence of hydrogen using $MgCl_2/TiCl_4/$ DNBP-$AlEt_3$/CHMDMS catalyst system at various polymerization temperatures. The results are shown in Table III. It can be seen that both the average isotactic index and the average mmmm value of the polymers produced without hydrogen have similar changing trends as those obtained in the presence of hydrogen. However, the catalyst activity in the absence of hydrogen is significantly lower than that with hydrogen for all five temperatures studied. Furthermore, when the catalyst activity value in the absence of hydrogen divide the corresponding value in the presence of hydrogen at the same polymerization temperature, it will get a deceleration factor which would be nearly constant under different polymerization temperatures. Therefore, adding a given amount of hydrogen would lead to similar acceleration effects at different active centers, which can be explained by that the same ratio of potentially active centers is always blocked in the absence of hydrogen.[28]

In light of above results, the effect of polymerization temperature on the reaction rate constant of different type active centers is considered as the major factor leading to the change of the average isotacticity of polymer. In both cases of the presence and absence of hydrogen, polymerization temperature has similar effect on the activity, and the activity of catalyst reaches a maximum value at the polymerization temperature of 85°C. On the contrary, the MWD value of polymer reaches a minimum at the of polymerization temperature of 85°C with or without hydrogen. It can hypothesize that in the catalyst system used above would possess a special type of active center. This type of active center performs a higher increase of activity with the polymerization temperature increasing from 70 to 85°C and a higher decrease of activity with the polymerization temperature above 85°C than other types of active centers, leading to narrow the MWD value at the polymerization temperature of 85°C.

Figure 5. Melting temperatures of Peak 1 and Peak 2 for the SSA curves of the samples obtained by different polymerization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
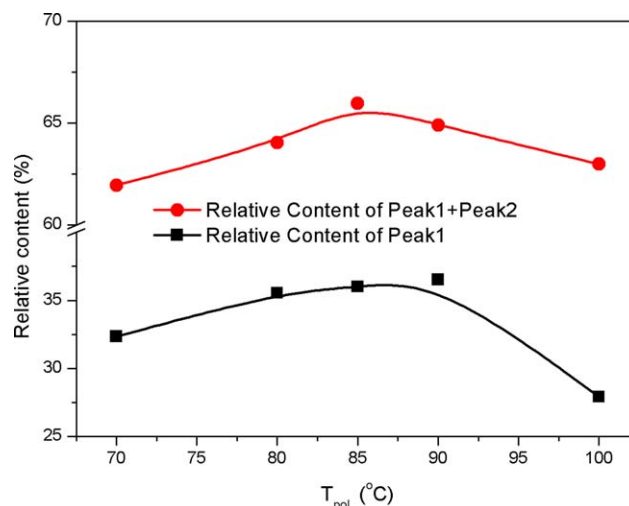
Figure 6. Variations of the relative contents of Peak 1 and Peak 1 + Peak 2 on the SSA fitted curves. The relative contents are the integral area percentages on the SSA fitted curves of samples obtained by different polymerization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Effects of the Polymerization Temperature on the Polymerization of Propylene Using MgCl$_2$/TiCl$_4$/DNBP-AlEt$_3$/CHMDMS Catalyst System Without Hydrogen

$T_{pol.}$	Activity	M_w	MWD	I.I.	mmmm
°C	KgPP/gcat h	×10^3		wt %	%
70	21.8	1402	8.47	98.2	89.0
80	25.2	1126	6.34	98.6	90.1
85	30.4	985	5.24	99.1	90.5
90	23.1	911	5.53	98.7	90.2
100	11.6	807	6.01	98.4	89.6

Table V. Effects of the Temperature on the Propylene Polymerization Using MgCl$_2$/TiCl$_4$/DIBDMP-AlEt$_3$ Catalyst System with a 0.3 mol % Hydrogen Concentration

$T_{pol.}$	Activity	M_w	MWD	I.I.	mmmm
°C	kgPP/gcat h	×10^3		wt %	%
70	63.8	162	5.25	94.5	92.3
80	85.5	133	4.63	96.1	92.9
85	100.2	128	3.69	96.9	93.5
90	99.6	117	3.60	97.6	93.5
100	53.2	98	4.10	94.4	93.1

At the same time, it can be assumed that this special type of active centers is the highest isotactic active centers, because they presented the more fitting ability of forming the complex with the donor for producing the polymer with highest isotacticity than other types of active centers under the same polymerization conditions. Based on the above analysis, it could try to explain the relation among the MWD values, the average isotactic indexes, the average mmmm values, and the nature of active centers. As the polymerization temperature increases, the increase of the activity of the highest isotactic active centers were higher than that of the other isotactic active centers in the polymerization temperature range of 70–85°C. This resulted in increasing of both the average isotactic indexes and the average mmmm values and narrowing the MWD values due to the major contribution of the component produced with the highest isotactic active centers. However, when the polymerizations temperature increased from 85 to 100°C, the decrease of the activity of the highest isotactic active centers would be higher than that of the others isotactic active centers. Thus, even if the activity of catalyst was sharply decreased, the MWD values would gradually increase with the polymerization temperature increasing. This is owing to that the proportion of component produced by the highest isotactic active centers was decreased. It could support that, from the data in Table II, the relative content of region A, the relative content of region B, and the relative content C gradually increase as the polymerization temperature increasing from 85 to 100°C, while the relative content of D is increased step by step above 85°C. In the meantime, the relative content of Peak1 + Peak2 also reaches the maximum value at the polymerization temperature of 85°C, as shown in Figure 6.

Table IV. Effects of the Temperature on the Propylene Polymerization Using MgCl$_2$/TiCl$_4$/DNBP-AlEt$_3$ Catalyst System with a 0.3 mol % Hydrogen Concentration

$T_{pol.}$	Activity	M_w	MWD	I.I.	mmmm
°C	kgPP/gcat h	×10^3		wt %	%
70	16.2	140	6.94	64.3	61.0
80	21.3	123	6.41	63.9	60.9
85	23.6	92	6.15	65.0	61.3
90	20.8	80	6.52	64.8	61.3
100	12.6	74	6.58	63.5	61.1

To obtain a better insight into the polymerizing performance of the catalyst systems under the different polymerization temperatures, a series of polymerizations were carried out without the external donor at various polymerization temperatures. The polymerization results of MgCl$_2$/TiCl$_4$/DNBP-AlEt$_3$ catalyst system with a 0.3 mol % hydrogen concentration are given in Table IV. The activity of catalyst system increases with the temperature increasing, and reaches a peak value at the polymerization temperature of 85°C. On contrast, the minimum of MWD values is observed at 85°C. Those results demonstrate that the reaction rate constant of different types of active centers is varied with the polymerization temperatures. In the absence of external donor, both the average isotactic indexes and the average mmmm values are approximately constant in the temperature range of 70–100°C. DNBP is nearly completely extracted by the cocatalyst during the course of polymerization, owing to the nucleophilic attack of the Al—C bond to the carbonyl group.[6,29] Thus, after the precontacting process—in which a fixed ratio of catalyst, cocatalyst, and external donor were pre-contacted before being injected into the reactor with pentane—the internal donor content of the catalyst did not change anymore because during polymerization, the cocatalyst concentration is much lower.[26] Sacchi et al. also found that when the diisobutyl phthalate catalyst contacts with different cocatalyst/external donor, the internal donor was nearly completely displaced.[30,31] The active centers without the donor lose their stereospecificity and produce atactic polymer[26] due to a reversible dissociation of the isospecific dinuclear Ti adducts.[32]

The stability constant of the complex of catalyst/donor is another factor to affect the stereoregularity of active centers.[22] In the absence of external donor, a catalyst containing a diether is studied as the internal donor at various polymerization temperatures. Table V shows the results of polymerizations using MgCl$_2$/TiCl$_4$/2,2-diisobutyl-1,3-dimethoxypropane (DIBDMP)-AlEt$_3$ catalyst system with a 0.3 mol % hydrogen concentration. The changing trends of both activity of catalyst system and MWD values of the polymers obtained using DIBDMP as the internal donor is the same as those obtained using DNBP. The changes of average isotactic index and average mmmm values of the polymers produced via DIBDMP as the internal donor with the polymerization temperature increasing, however, are similar as those produced with the catalyst system containing DNBP as the internal donor in the presence of external donor. This is due to that only trace amounts of DIBDMP internal donor are

Table VI. Effects of the Temperature on the Propylene Polymerization Using $MgCl_2$/$TiCl_4$/DNBP-$AlEt_3$/DCPDMS Catalyst System with a 0.3 mol % Hydrogen Concentration

$T_{pol.}$	Activity	Mw	MWD	I.I.	mmmm
°C	KgPP/g cat h	$\times 10^3$		wt %	%
70	56.2	346	6.47	97.5	93.5
80	62.5	316	6.01	98.6	94.3
85	65.3	293	5.15	98.8	94.6
90	57.3	261	5.26	98.5	94.1
100	31.6	228	5.98	98.0	93.8

extracted from the catalyst surface during the polymerization process.[23,29] This supports the above hypothesis that highest isotactic active centers, which presented a more fitting ability of forming complex with the donor for producing highest isotactic polymer than other types of active centers under the same polymerization conditions, were sensitive for changed polymerization temperatures.

With addition of external donor, the position in which the internal donor was absorbed at first and then the external donor was absorbed should be, at least for some active centers, close enough to the active Ti to affect the stereochemistry of the monomer insertion.[30] The donor can saturate the coordination vacancy of the Mg atoms adjacent to the isospecific dinuclear adduct to avoid the reversible dissociation of the isospecific dinuclear Ti adducts.[23,32]

To investigate the effect of the stability constant of the complex of catalyst/external donor on the isotaciticity of product, the polymerization was carried out with another external donor, dicyclopentyl dimethoxy silane (DCPDMS), in the polymerization temperature range from 70 to 100°C. The polymerization results of $MgCl_2$/$TiCl_4$/DNBP-$AlEt_3$/DCPDMS catalyst system with a 0.3 mol % hydrogen concentration are shown in Table VI. The bulky hydrocarbyl groups of external donor can protect the external donor from leaving the catalyst surface via complexation with the alkylaluminium.[33,34] Since the bulkiness of hydrocarbyl groups of DCPDMS is larger than that of CHMDMS, it is more difficult for the alkylaluminium to approach DCPDMS than to approach CHMDMS. Therefore, the stability constant of the DCPDMS/catalyst complex for producing high-isotactic polymer is higher than that of the CHMDMS/catalyst complex under the same polymerization conditions. As a result, using DCPDMS as the external donor gives the polymer with higher isotacticity. It is also noted that the variation of the isotacticity index value of the polymer is small with the polymerization temperature changing due to stable stability constant of DCPDMS/catalyst complex.

CONCLUSIONS

The effect of polymerization temperature on the microstructure of isotactic polypropylene is investigated with a number of different catalyst systems in the polymerization range from 70 to 100°C in the presence and absence of hydrogen. In all experiments, the highest activities and narrowest of MWD are obtained

at the polymerization temperature of 85–90°C. The polypropylene samples obtained at 85–90°C contain the higher content of the polymer component with highest isotacticity than other samples for the $MgCl_2$/$TiCl_4$/DNBP-$AlEt_3$/external donor and $MgCl_2$/$TiCl_4$/DIBDMP-$AlEt_3$ catalyst systems in the absence or presence of hydrogen. The differences in the isotactic productivity of polymers obtained at different polymerization temperatures mainly result from the variation of both the activity of the different isospecific active centers and the stability constants of the complex of catalyst/donor. For the $MgCl_2$/$TiCl_4$/DNBP-$AlEt_3$ catalyst system, the isotacticity of polypropylene is constant in the temperature range of experiments. This can be ascribed to elution of DNBP after the activation.

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