Influence of "TMA-depleted" MAO and alkylaluminiums on propylene polymerization at high temperature with TiCl$_4$/MgCl$_2$ catalysts

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Abstract

A study of the effect of "trimethylaluminium (TMA)-depleted" methylaluminoxane (MMAO) and alkylaluminiums on propylene polymerization at high temperature in the use of a TiCl$_4$/MgCl$_2$/aromaticdiester-alkoxysilane catalyst has shown that, MMAO was not the actual cocatalyst. However, at low Et$_3$Al/Ti mole ratio addition of MMAO to catalyst improved the catalyst activity and stereospecificity and the catalyst showed a high proportions of isotactic polypropylene (95%) and high activity with the mixture of MMAO and Et$_3$Al at 100 °C. Addition of MMAO reduced the molecular weights of isotactic polypropylene (iPP) but had no effect on the crystallinity of the iPPs. The appearance of β modification in the iPP obtained with Et$_3$Al crystallization process implied that the microstructure of iPP obtained with Et$_3$Al was different from that of iPP obtained with i-Bu$_3$Al and Hex$_3$Al at 100 °C.
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1. Introduction

High-activity MgCl$_2$-supported Ziegler–Natta catalysts, in which the solid catalyst comprises TiCl$_4$, MgCl$_2$ and electron donors, play a dominant role in poly(propylene) (PP) manufacture. It is well known that the industrial polymerization temperature of MgCl$_2$-supported Ziegler–Natta catalysts are around 65–80 °C. In recent years, a new supercritical olefin polymerization technology was developed, which needed higher polymerization temperature (more than 90 °C) for propylene polymerization. However, both the activity and the stereospecificity of MgCl$_2$-supported Ziegler–Natta catalysts decease when the polymerization temperature rises over 85 °C [1,2]. Kojoh et al. [1] and our research group [3] had reported that in the propylene polymerization with MgCl$_2$-supported Ziegler–Natta catalysts at 100 °C, the activity obtained with i-Bu$_3$Al, which shows a weaker coordination

and alkylation than Et$_3$Al, was higher than that obtained with Et$_3$Al.

The use of alkylaluminiums as an activating agent is indispensable for propylene polymerization with MgCl$_2$-supported Ziegler–Natta catalysts. Many investigations concerning the effect of alkylaluminiums on the propylene polymerization with Ziegler–Natta catalyst have been conducted in academic and industrial fields [2].

In our previous communication [4], we have reported that the TiCl$_4$/MgCl$_2$/9,9-bis(methoxymethyl)fluorine catalyst was inactive with "trimethylaluminium (TMA)-depleted" methylaluminoxane (MMAO) in propylene polymerization. Methylaluminoxane (MAO) is a powerful activator for group IV metallocenes in the field of olefin polymerization catalysis [5–8]. Despite intense interest from both academic and industrial laboratories, the structure and function of MAO is not well understood [6]. In this paper, we first reported the TiCl$_4$/MgCl$_2$/dibutyl phthalate (DNBP)-cyclohexyl(methyl)dimethoxysilane (CHMDMS) catalyst showed high proportions of isotactic polypropylene and high activity with the mixture of MMAO and Et$_3$Al at 100 °C.

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The influences of the cocatalyst on the results of propylene polymerization at 100 °C were investigated here.

2. Experimental part

2.1. Preparation of TiCl₄/MgCl₂/DNBP catalyst

The catalyst containing DNBP as the internal donor was prepared according to ref. [9]. The content of titanium in the catalyst was 2.6 wt.%.

2.2. Preparation of MMAO

In a typical experiment, 20 ml of MAO (10 wt.% as toluene solution, Witco) were dried under vacuum at room temperature. The resulting white gel was then heated at 80 °C under vacuum for 5 h to distillated trimethylaluminium.

2.3. Propylene polymerization

In a 400 ml reactor previously purged with nitrogen and propylene, 150 ml anhydrous *n*-decane was added. MMAO was first added and then the mixture of a prescribed amount of catalyst (30–50 mg) and other components were also added at room temperature. The reactor was rapidly raised to desired polymerization temperature. Polymerization was carried out under pressure in the range 0.11–0.13 MPa. The reaction time was 1 h. The polymer was filtered and dried. A sample from the liquid phase was taken to determine the amount of dissolved polymer.

2.4. Polymer analyses

Polypropylene was fractionated with boiling heptane by conventional methods. Titanium content of the catalyst was measured on a 722 spectrophotometer. The thermal analysis was carried out by means of DSC (Perkin-Elmer DSC-7). The isotactic polypropylene sample was heated to 200 °C and held in the molten state for 5 min to eliminate the influence of thermal history. The sample melts was then subsequently quenched at a rate of 200 °C/min to reach 125 °C for isothermal crystallization for 30 min. Then the sample was heated at 10 °C/min again.

The molecular weight of iPP was measured by polymer lab. PL-GPC220. The weight-average and number-average molecular weight (M_w and M_n, respectively) of iPP were calculated on the basis of a polystyrene standard calibration. ^{13}C NMR spectra of iPPs were recorded with a Bruker DMX 400 spectrometer operating at 100.6 MHz, on 10 mg/ml solutions in deuterated dichlorobenzene at 110 °C. Condition: 10 mm probe; acquisition time, 5 s; relaxation time, 10 s; numbers of scans 5000. ^{1}H NMR spectra of MAO and MMAO were recorded with a Bruker av 300 spectrometer operating at room temperature. Wide-angle X-ray diffraction was obtained at room temperature with an automatic Philips diffractometer (X'Pert, MPD).

3. Results and discussion

3.1. Effect of MMAO and alkylaluminiums on the catalyst activity and stereospecificity

Commercial MAO solution contains a high percentage of trimethylaluminium (30–35%) remaining from its hydrolysis process. The ^{1}H NMR spectrum of MMAO (Fig. 1) shows that the peak (−0.36 ppm) attributed to free TMA [7] has been greatly reduced. It showed MMAO contained no or very little free TMA.

The results obtained with MMAO and alkylaluminiums in the propylene polymerization with TiCl₄/MgCl₂/DNBP-CHMDMS catalyst system at 100 °C were shown in Table 1. It was clear that an increase in polymerization temperature led not only to lower activity of catalyst but also to lower stereospecificity when alkylaluminiums were used as cocatalyst. It could be due to over reduction of titanium or to reactions of Ti–C bonds with Lewis base [2]. At 100 °C, the catalyst activity obtained with either *i*-Bu₃Al or Hex₃Al was higher than that obtained with Et₃Al while isotacticity of PP obtained with either *i*-Bu₃Al or Hex₃Al was lower than that obtained with Et₃Al. With increasing Al/Ti ratio at 100 °C, both stereospecificity and activity of the catalyst decreased. It was worth noting that the catalyst in the presence of the commercial MAO which contains a high percentage of trimethylaluminium (30–35%) showed low proportions of isotactic polypropylene at 100 °C, as opposed to TiCl₄/MgCl₂/9,9-bis(methoxymethyl)fluorine catalyst [4].
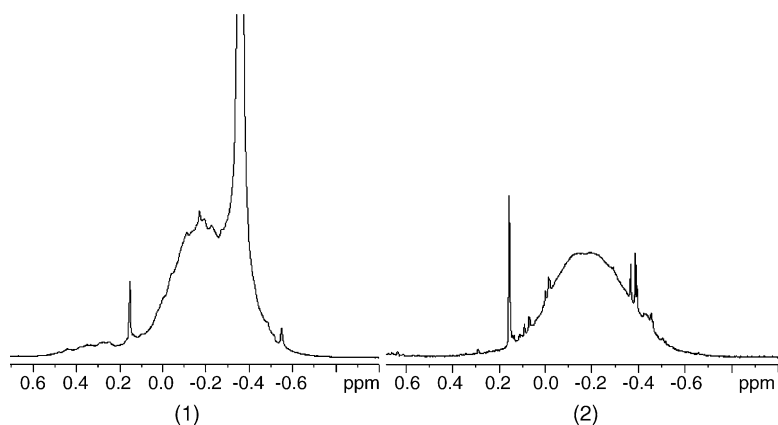

Fig. 1. ^{1}H NMR spectra in toluene *d*-8 of commercial MAO (1) and of MMAO (2) ("TMA-depleted" MAO).

Table 1
Results of propylene polymerization with MgCl$_2$/TiCl$_4$/DIBP catalyst at 100 °C[a]

Run	Cocatalyst	Activity ($\times 10^{-3}$) (g PP/g Ti h)	I.I.[b] (%)	ΔH_f (J/g)	Melting point (°C)
1	Et$_3$Al/Ti = 50[c]	9.6	94	97.7	163.7
2	Et$_3$Al/Ti = 25	6.2	92	97.2	163.2
3	Et$_3$Al/Ti = 50	6.6	90	99.8	162.4
4	Et$_3$Al/Ti = 150	4.6	81	96.8	161.4
5	i-Bu$_3$Al/Ti = 50	12.9	80	89.5	161.0
6	i-Bu$_3$Al/Ti = 150	8.6	77	88.8	161.4
7	Hex$_3$Al/Ti = 50	9.3	65	81.8	159.5
8	Hex$_3$Al/Ti = 150	7.2	56	81.6	159.7
9	MAO/Ti = 50	7.2	76	83.4	160.5
10	MMAO = 50	_[d]	–	–	–
11	Et$_3$Al/Ti = 25 MMAO/Ti = 50	9.6	94	94.3	161.6
12	Et$_3$Al/Ti = 25 MMAO/Ti = 25	11.0	95	93.4	162.7
13	Et$_3$Al/Ti = 50 MMAO/Ti = 50	7.5	78	95.4	161.0
14	i-Bu$_3$Al/Ti = 50 MMAO/Ti = 50	12.0	81	92.9	161.4
15	Hex$_3$Al/Ti = 25 MMAO/Ti = 50	11.8	73	84.4	159.9

[a] Polymerization conditions: propene pressure = 0.11–0.13 MPa, catalyst = 30–50 mg, ex-donor: CHMDMS, Al/Si = 20.
[b] Isotacticity index: weight percent of heptane-insoluble fraction.
[c] Polymerization temperature: 70 °C.
[d] No polymer was obtained.

It is apparent, as observed from TiCl$_4$/MgCl$_2$/9,9-bis(methoxymethyl)fluorine catalyst previously [4], that the TiCl$_4$/MgCl$_2$/DNBP-CHMDMS catalyst had no activity in the presence of MMAO that contained no or very little free TMA. Additions of alkylaluminiums, such as Et$_3$Al, i-Bu$_3$Al and Hex$_3$Al to MMAO caused high activity. MMAO is not the actual cocatalyst in propylene polymerization. At the same time, we observed that in the ethylene polymerization at 70 °C the TiCl$_4$/MgCl$_2$/9,9-bis(methoxymethyl)fluorine catalyst had very low activity with MMAO and the resultant polyethylene had low melting point (126.0 °C). It indicated that MMAO is a cocatalyst in the ethylene polymerization. Based on the results obtained from metallocene catalysts [5–8,10–13], we propose that alkylation reaction of TiCl$_4$ with MMAO takes place but a tight ion pair between MMAO and titanium species that is inefficient for the activation of propylene polymerization was formed when only MMAO was added [4].

It is interesting that at Et$_3$Al/Ti mole ratio 25 addition of MMAO caused an increase in the catalyst activity and stereospecificity at 100 °C (Run 12), which were even higher than those obtain with Et$_3$Al at 70 °C (Run 1). However, at Et$_3$Al/Ti mole ratio 50 addition of MMAO caused a decrease in the catalyst stereospecificity. At low Hex$_3$Al/Ti addition of MMAO also caused an increase in the catalyst activity and stereospecificity at 100 °C. At i-Bu$_3$Al/Ti mole ratio 50 addition of MMAO had almost no effect on the catalyst activity and stereospecificity at 100 °C. Since MMAO is not the actual cocatalyst, one possible function of MMAO in the catalyst system is that the presence of MMAO can stabilize the active sites or avoid contamination by poisons accidentally present in the system when triethylaluminium concentration is low. High triethylaluminium concentration could lead to rapid decay of polymerization rate at high temperature.

3.2. Effect of MMAO and alkylaluminiums on polymer properties

Table 2 showed the weight average molecular weight (M_w) and molecular weight distribution (MWD) obtained with the corresponding iPP samples (heptane-insoluble fraction of polypropylene). As shown in Table 2, with increasing R$_3$Al/Ti ratio at 100 °C, the molecular weights of iPPs obtained with Et$_3$Al dropped fast while those obtained with either i-Bu$_3$Al or Hex$_3$Al slightly decreased.

MAO is not efficient transfer agent on propylene polymerization with metallocene [7]. It is well known that in the absence of hydrogen and under normal polymerization conditions, transfer with monomer is the most important chain termination process in propylene polymerization with heterogeneous catalysts and chain transfer with the cocatalyst plays a secondary role [7]. However, chain transfer with the cocatalyst played a primary role in our experiments because the concentration of

Table 2
GPC and DSC results of propylene polymerization with cocatalysts at 100 °C

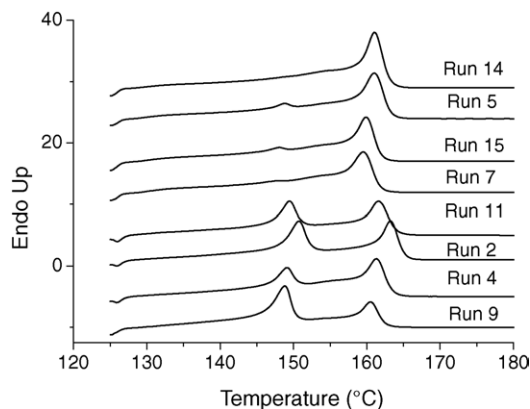| Cocatalyst	M_w ($\times 10^{-3}$) (g/mol)	M_w/M_n
Et$_3$Al/Ti = 50	224	5.2
Et$_3$Al/Ti = 150	155	5.5
Et$_3$Al/Ti = 50 MMAO/Ti = 50	154	4.5
Et$_3$Al/Ti = 25 MMAO/Ti = 25	358	5.5
Et$_3$Al/Ti = 25 MMAO/Ti = 50	234	4.5
Et$_3$Al/Ti = 5 MMAO/Ti = 50	418	4.3
i-Bu$_3$Al/Ti = 50	366	4.9
i-Bu$_3$Al/Ti = 150	291	4.7
i-Bu$_3$Al/Ti = 50 MMAO/Ti = 50	268	4.1
Hex$_3$Al/Ti = 50	331	4.1
Hex$_3$Al/Ti = 150	288	4.0
Hex$_3$Al/Ti = 5 MMAO/Ti = 50	545	4.5
Hex$_3$Al/Ti = 25 MMAO/Ti = 50	275	3.7

Fig. 2. Comparison of melting curves subsequent to crystallization at 125 °C, heating rate is 10 °C/min.

Table 3
Steric pentad composition of iPPs

Run	mmmm	mmmr	rmmr	mmrr	mmrm + rmrr	rmrm	rrrr	rrrm	mrrm
2	92.9	2.8	0.3	1.7	0.8	0	0.5	0.4	0.6
4	91.2	3.5	0.4	1.8	1.2	0.2	0.5	0.5	0.7
11	91.6	3.0	0.1	2.5	0.8	0	0.4	0.6	1.0

cocatalyst was much higher than that in normal polymerization conditions.

It was worth noting that at the same ratio of R_3Al to Ti addition of MMAO reduced the molecular weight of iPP. One of the probable interpretations of it was that Me–R (Et, i-Bu, Hex) exchange reaction would take place when MMAO was added to alkylaluminium at 100 °C and in fact some of the cocatalyst was MeR_2Al, which may be a more efficient chain transfer agent.

Fig. 2 shows the melting curves for iPP samples after isothermal crystallization at 125 °C. The melting point and the enthalpy

of fusion (ΔH_f) was showed in Table 1. The iPPs obtained with Et_3Al at 100 °C exhibited bimodal peaks, and one was in the vicinity of 160 °C and the other was in the vicinity of 150 °C. The iPP obtained with the commercial MAO containing a high percentage of TMA (30–35%) also exhibited bimodal peaks (Run 9). In contrast, the iPPs obtained with either i-Bu_3Al or Hex_3Al had very small peak or no peak in the vicinity of 150 °C. Addition of MMAO to the alkylaluminium had no effect on the crystallinity of the polypropylene, as reported previously [4].

The ^{13}C NMR analysis was then conducted to obtain information on the microstructure of the present samples obtained with Et_3Al. The pentad distributions of these iPPs, which are calculated from the methyl region resonance, are listed in Table 3. As shown in Table 3, the [mmmm] pentad content of the iPPs decreased with increasing Et_3Al/Ti ratio at 100 °C. The addition of MMAO also caused the [mmmm] pentad content slightly lower.
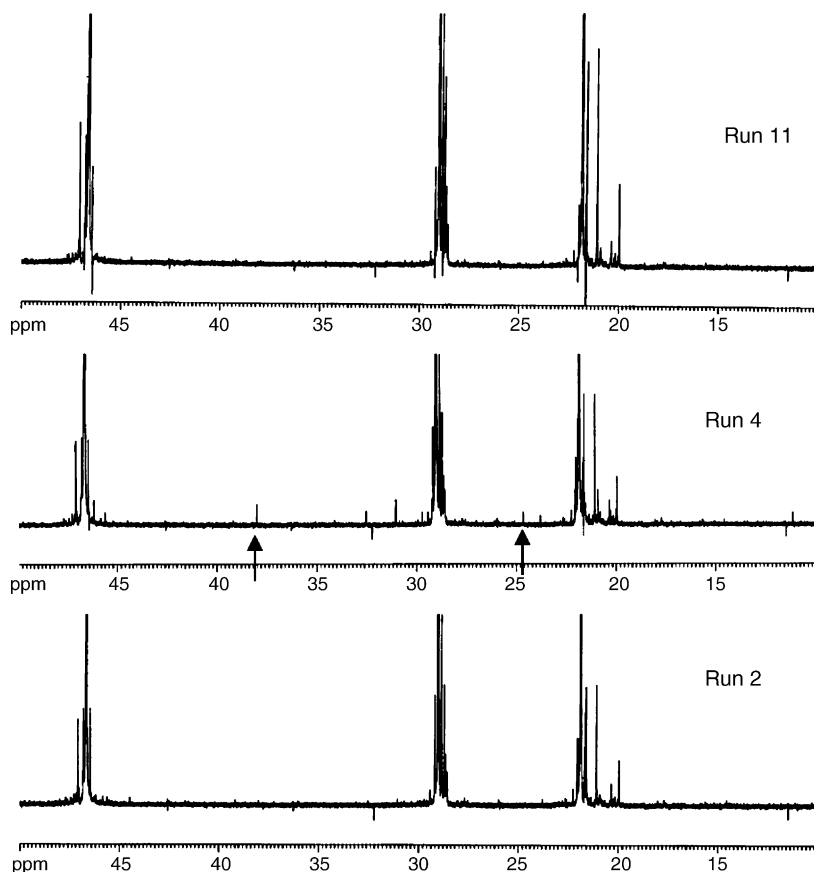

Fig. 3. ^{13}C NMR spectra of the iPP samples.

The ^{13}C NMR spectra of iPPs of Runs 2, 4 and 11 were shown in Fig. 3. The spectrum of Run 4 showed a number of small irregular peaks. The samples that contained ethylene units would show the peak (38.0 ppm, $\alpha\gamma$-CH$_2$), the peak (31.0 ppm, $\beta\delta$-CH) and the peak (24.6 ppm, $\beta\beta$-CH$_2$) in the correct 2:2:1 integral ratio [1,14]. Investigation of Kojoh et al. [1] and our group [14] showed that the ethylene arose from the degradation of Et$_3$Al at 100 °C. It was clear that at Et$_3$Al/Ti mole ratio 150 (Run 4) the iPP contained ethylene unit (0.1%, mol%), while at Et$_3$Al/Ti mole ratio 25 (Run 2), the iPP contained scarcely ethylene unit. As shown in Fig. 2, both Runs 4 and 2 exhibited bimodal endothermic peak. It implied that the peak of 150 °C showed in DSC was not the result of ethylene copolymerization. We suggested the bimodal melting behavior could arise from tacticity effects.

Investigations of Terano and co-workers suggested that the isospecific active sites produced by various trialkylaluminiums are identical, but the number and the ratio of active sites are different [15]. It implied that the difference of these isotactic poly(propylene)s obtained with trialkylaluminiums could be only explained by the difference of external donors existed in the polymerization system. Investigations of Sacchi et al. [16] and Terano and co-workers [17] showed that the number of alkoxy groups attached to a silane atom could play an important role as a critical parameter for stereospecificity of the catalyst and the presence of more alkoxy groups made the alkoxy silane more effective in selecting poisoning. Investigations of Vahasarja et al. [18] had illustrated that the complexation of silyl ether and Et$_3$Al is unstable and the complex undergoes alkylation at 75 °C. Therefore, the resultant silyl ether–Et$_3$Al complexes could have an influence on stereospecificity of the catalyst at 100 °C, which resulted in iPP produced of different distribution of isospecificity. The complex of silyl ether and either Hex$_3$Al or i-Bu$_3$Al may be stabler than that of silyl ether and either Et$_3$Al or Me$_3$Al.

The results of WAXD for these iPPs are displayed in Fig. 4, and these results were obtained under the same experimental conditions: the samples first was immersed in a silicone oil bath at 200 °C for 6 min, and then quickly turned to another silicone oil hot bath at 125 °C for 30 min. The characteristic peak at 16° was attributed to β modification (300) of iPP. As showed in Fig. 4, the iPPs obtained with Et$_3$Al (Runs 3 and 13) at 100 °C exhibited the characteristic peak at 16° while this phenomenon for the iPP obtained with either i-Bu$_3$Al (Runs 5 and 14) or Hex$_3$Al (Runs 7 and 15) cannot be distinguished. Obviously, the WAXD results were in agreement with the DSC aforementioned observation. The formation of β modification is closely related to the intrinsic polymer characteristics, i.e., the isotactic sequence length of the component with certain molecular chain lengths and distribution of stereo- and regioregularity [19,20]. It implied that the microstructure of iPP obtained with Et$_3$Al was different from that of iPP obtained with i-Bu$_3$Al and Hex$_3$Al at 100 °C. The correlation between the formation of β modification and microstructure characteristics of molecular chains is in progress.

4. Conclusions

In this paper, we have reported that the TiCl$_4$/MgCl$_2$/DNBP-CHMDMS catalyst had no activity in the presence of MMAO containing no or very little free TMA in propylene polymerization. Additions of alkylaluminiums, such as Et$_3$Al, i-Bu$_3$Al and Hex$_3$Al to MMAO caused high activity. MMAO was not the actual cocatalyst in propylene polymerization. However, at low Et$_3$Al/Ti mole ratio additions of MMAO improved the activity and stereospecificity of the catalyst at 100 °C and the catalyst showed a high proportions of isotactic polypropylene and high activity with the mixture of MMAO and Et$_3$Al at 100 °C. Addition of MMAO reduced the molecular weight of iPPs but had no effect on the crystallinity of the iPPs. The appearance of β modification in the iPP obtained with Et$_3$Al crystallization process implied that the microstructure of iPP obtained with Et$_3$Al was different from that of iPP obtained with i-Bu$_3$Al and Hex$_3$Al at 100 °C.

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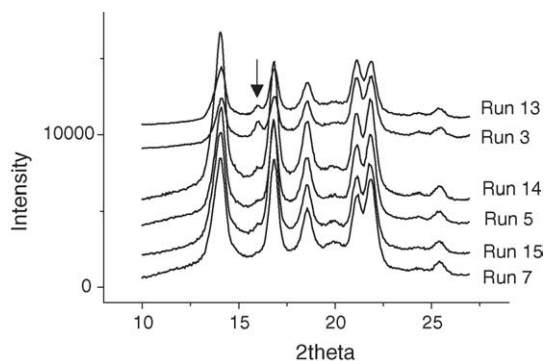[15] H. Nori, H. Iguchi, K. Hasebe, M. Terano, Macromol. Chem. Phys. 198 (1997) 1249.

Fig. 4. The WAXD evidence of β modification for Runs 3 and 13. The experiments were conducted under the same condition: after holding 200 °C for 6 min, quickly turning the sample to a hot bath at 125 °C for 30 min.

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