

# Effect of High Polymerization Temperature on the Microstructure of Isotactic Polypropylene Prepared Using Heterogeneous $\text{TiCl}_4/\text{MgCl}_2$ Catalysts

Chifeng Zhong,<sup>1</sup> Mingzhi Gao,<sup>2</sup> Bingquan Mao<sup>2</sup>

<sup>1</sup>State Key Lab of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, China

<sup>2</sup>Beijing Research Institute of Chemical Industry, Beijing, 100013, China

Received 12 December 2002; accepted 24 February 2003

**ABSTRACT:** The effects of alkylaluminum and polymerization temperature on propylene polymerization without an external donor in the use of a  $\text{TiCl}_4$ - $\text{MgCl}_2$ -diether(BMMF) catalyst were investigated. The results indicated that with increasing polymerization temperature the concentrations of [mmmm] of heptane-insoluble poly(propylene) (PP) fraction increased. Crystallization analysis fractionation (CRYSTAF) results showed the fractions of different crystallization temperatures were changed according to various polymerization temperatures. The activity with  $\text{Et}_3\text{Al}$  as cocatalyst at 100°C was much lower than that at 70°C. However, the activity with *i*- $\text{Bu}_3\text{Al}$  at 100°C was as high as that at 70°C. The fraction of high-crystallization temperature of PPs ob-

tained with *i*- $\text{Bu}_3\text{Al}$  increased with increasing polymerization temperature, which was opposite to that with  $\text{Et}_3\text{Al}$ , thus implying that the copolymerization of propylene with the monomer arising from  $\text{Et}_3\text{Al}$  led to the lower crystallization ability of PPs obtained with  $\text{Et}_3\text{Al}$ . The terminal groups of PP suggested that the chain-transfer reaction by  $\beta$ -H abstraction was the main chain-transfer reaction at 120°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3980–3986, 2003

**Key words:** poly(propylene) (PP); Ziegler–Natta polymerization; microstructure; crystallization; catalysts

## INTRODUCTION

It is well known that the industrial polymerization temperatures of  $\text{MgCl}_2$ -supported Ziegler–Natta catalysts are around 70–80°C. The polymerization temperature at higher temperature (>80°C) is desired industrially to reduce the burden of removing the heat of polymerization in the commercial plants. In recent years a new supercritical olefin polymerization technology was developed, which also required higher polymerization temperature (>90°C) for propylene polymerization. However, both the activity and the stereospecificity of  $\text{MgCl}_2$ -supported Ziegler–Natta catalysts decrease when the polymerization temperature rises over 80°C.<sup>1</sup> Kojoh et al.<sup>1</sup> reported that the activity and molecular weight dropped by increasing polymerization temperature, although, in the propylene polymerization at 100°C using a  $\text{MgCl}_2$ - $\text{TiCl}_4$ -dioctylphthalate catalyst in combination with alkylaluminum and diphenyldimethoxysilane, the activity and molecular weight with *i*- $\text{Bu}_3\text{Al}$  was higher than that with  $\text{Et}_3\text{Al}$ . Hoeg and Liebman (cited in Boor<sup>2</sup>) reported in propylene polymerization from 75 to 175°C using a  $\text{TiCl}_3$ - $\text{AlR}_3$  catalyst system, the propor-

tions of isotactic polymer with  $\text{Et}_3\text{Al}$  were higher than with *i*- $\text{Bu}_3\text{Al}$ .

To determine the effect of polymerization temperature on activity and microstructure, we carried out polymerizations with a catalyst system prepared by the method described in Mao et al.,<sup>3</sup> ranging from 50 to 120°C. We used a novel catalyst containing the internal donors 9,9-bis(methoxymethyl)fluorine (BMMF), which can obtain high activity and isospecificity without external donors.<sup>4</sup> The investigation was simplified because we did not need to consider the reaction between internal and external donors at high temperature.

## EXPERIMENTAL

### Preparation of $\text{TiCl}_4$ - $\text{MgCl}_2$ -BMMF catalyst

The catalyst containing BMMF as the internal donor was prepared according to Mao et al.<sup>3</sup> The titanium content in the catalyst was 1.9 wt %.

### Propylene polymerization

In a 400-mL reactor previously purged with nitrogen and propylene, 200 mL anhydrous *n*-decane was added. Then, a prescribed amount of catalyst (50–70 mg) and  $\text{Et}_3\text{Al}$  were added at room temperature. The reactor temperature was rapidly increased to the desired polymerization temperature. Polymerization

Correspondence to: B. Mao (maobingquan@brici.ac.cn).

TABLE I  
Results of Propylene Polymerization with Et<sub>3</sub>Al at Various Temperatures<sup>a</sup>

Run	T (°C)	Al/Ti (mol/mol)	Activity × 10 <sup>-3</sup> (gPP/g Ti h)	I · I <sup>b</sup> (%)	M <sub>w</sub> (× 10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub>	M <sub>p</sub> <sup>c</sup> (°C)	ΔH <sub>f</sub> (J/g)
1	50	50	16.3	96.	53.4	4.61	—	—
2	70	50	21.2	96.0	24.6	5.47	158.7	89.1
3	70	150	17.6	92.3	16.7	5.87	—	—
4	70	300	16.1	87.5	14.1	5.6	157.9	93.2
5	100	50	13.1	95.1	38.0	4.62	160.4	84.9
6	100	150	10.7	84	12.3	6.82	158.2	95.4
7	120	50	7.0	77	13.4	7.88	158.5	98.4

<sup>a</sup> Polymerization conditions: catalyst = 50–70 mg, *n*-decane (heptane) = 200 mL, time = 1 h, propene pressure = 1.2–1.4 × 10<sup>5</sup> Pa.

<sup>b</sup> Weight percent of heptane-insoluble fraction.

<sup>c</sup> Melting temperatures (second fusion, rate 10°C/min) and ΔH<sub>f</sub> measured by DSC.

was carried out under pressure in the range 0.11–0.13 MPa, for a reaction time of 1 h. The polymer was filtered and dried. A sample from the liquid phase was taken to determine the amount of dissolved polymer. At least two experiments were performed with the same polymerization conditions. Isotacticity index and productivity were average values.

#### Polymer analyses

Polypropylene was fractionated with boiling heptane by conventional methods. The titanium content of the catalyst was measured on a 722 spectrophotometer (Shanghai Analytical Instrument Overall Factory, China). Melting points of the polymers were measured by means of DSC (Perkin–Elmer DSC-7; Perkin Elmer Cetus Instruments, Norwalk, CT) by heating from 50 to 210°C at a heating rate of 10°C/min. The molecular weight of poly(propylene) (PP) was measured by a Waters gel permeation chromatograph Alliance GPCV 2000 (Waters Chromatography Division/Millipore, Milford, MA). The weight-average and number-average molecular weights (M<sub>w</sub> and M<sub>n</sub>, respectively) of polymers were calculated on the basis of a polystyrene standard calibration. <sup>13</sup>C-NMR spectra of PPs were recorded with a Bruker DMX 400 spectrometer (Bruker Instruments, Billerica, MA) operating at 100.6 MHz, on 10–20 mg/mL solutions in deu-

terated dichlorobenzene at 110°C (conditions: 5-mm probe; pulse repetition 4 s, numbers of scans 20,000). A crystallization analysis fractionation (CRYSTAF) was performed by a CRYSTAF apparatus, model 200, from Polymer Char S.A. (Valencia, Spain). Samples of about 30 mg were dissolved in 30 mL distilled 1,2,4-trichlorobenzene at 160°C for 2 h. The temperature was decreased at a rate of 0.1°C/min between 160 and 65°C. Fractions were taken automatically and the polymer concentration in solution was determined by an infrared detector using 3.5 μm as the measuring wavelength.

#### RESULTS AND DISCUSSION

Results of the propylene polymerizations with diether(BMMF)-containing catalyst in the range of 70–120°C using Et<sub>3</sub>Al as cocatalyst are shown in Table I; results using *i*-Bu<sub>3</sub>Al are shown in Table II, along with the isotactic PP molecular weight distributions determined by GPC and melting point and the enthalpy of fusion (ΔH<sub>f</sub>) by DSC. It was clear that an increase in temperature led not only to lower proportions of the isotactic fraction but also to the decreased molecular weight. However, in the polymerization with Et<sub>3</sub>Al (Al/Ti = 50, molar ratio), the molecular weight at 100°C was higher than that at 70°C, which implied that at a lower concentration of Et<sub>3</sub>Al, the molecular

TABLE II  
Results of Propylene Polymerization with *i*-Bu<sub>3</sub>Al at Various Temperatures

Run	T (°C)	Al/Ti (mol/mol)	Activity × 10 <sup>-3</sup> (gPP/g Ti h)	I · I (%)	M <sub>w</sub> (× 10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub>	M <sub>p</sub> (°C)	ΔH <sub>f</sub> (J/g)
8	50	50	12.2	94.6	94.6	4.96	—	—
9	70	50	21.9	96.7	74.7	5.05	158.2	77.3
10	70	150	27.1	96	54.7	4.44	157.7	76.2
11	70	300	27.6	95.7	51.8	4.75	158.4	77.3
12	100	50	22.0	90.0	36.0	4.12	160.0	80.3
13	100	150	27.0	91.5	38.8	4.31	160.5	86.4
14	120	50	7.1	78	26.1	5.25	160.5	91.2

TABLE III  
Steric Pentad Composition (in mol %) of Polypropylene with Different Samples

Pentad	Run 2 <sup>a</sup> (70°C)	Run 11 (70°C)	Run 6 (100°C)	Run 13 (100°C)	Run 7 (120°C)	Run 14 (120°C)
mmmm	92.2	89.7	93.7	93.5	94.9	95.4
mmmr	2.3	3.7	2.3	2.4	2.8	2.8
rmmr	0.7	0.4	0.6	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
mmrr	2	2.5	1.4	1.8	1.2	1.3
mrmr + rmrr	0.8	1.1	0.7	0.6	0.6	— <sup>b</sup>
rmmr	— <sup>b</sup>	0	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>	— <sup>b</sup>
rrrr	0.6	0.8	0.5	0.5	0.1	— <sup>b</sup>
rrrm	0.5	0.7	0.3	0.5	— <sup>b</sup>	— <sup>b</sup>
mrrm	0.8	1.2	0.5	0.6	0.4	0.5

<sup>a</sup> Number of scans was 10,000, not 20,000.

<sup>b</sup> Too weak for accurate integration.

weight of the isotactic fraction could increase with increasing polymerization temperature. Chadwick et al.<sup>5</sup> proposed that a higher polymerization temperature could effectively reduce the barrier to chain propagation after 2,1-insertion for diether-containing catalysts.

The molecular weight of PPs obtained with Et<sub>3</sub>Al decreased rapidly when the concentration of Et<sub>3</sub>Al was increasing at 100°C. However, the molecular weight of PPs obtained with *i*-Bu<sub>3</sub>Al was identical when the concentration of *i*-Bu<sub>3</sub>Al was increasing. These results are in accordance with the study reported by Kojoh et al.<sup>1</sup>

In the polymerization with *i*-Bu<sub>3</sub>Al, when the molar ratio of Al to Ti increased from 50 to 150, the activity at 100°C was essentially the same with that at 70°C. It can be reasoned that a weaker complexation between the internal donor (BMMF) and *i*-Bu<sub>3</sub>Al, as opposed to Et<sub>3</sub>Al, will lead to less loss of internal donor in the catalyst even when the polymerization temperature is 100°C, which suggests that *i*-Bu<sub>3</sub>Al is a suitable cocatalyst in propylene polymerization at the higher temperature.

When the polymerization temperature was increased to 120°C, the isotactic fraction and activity were the same by use of either Et<sub>3</sub>Al or *i*-Bu<sub>3</sub>Al; however, the molecular weight of the PP obtained with *i*-Bu<sub>3</sub>Al was higher than that with Et<sub>3</sub>Al.

It is apparent from Tables I and II that increasing temperature leads to higher enthalpy of fusion ( $\Delta H_f$ ) of these isotactic PPs. It is well known that  $\Delta H_f$  depends on the degree of crystallinity. Thus the degree of crystallization of the isotactic PP increased with increasing polymerization temperature. <sup>13</sup>C-NMR and crystallization analysis are two major methods of studying the microstructure of PP. The isotactic PPs in Tables I and II were selected for <sup>13</sup>C-NMR analysis. The pentad distributions of these isotactic PPs, which are calculated from the methyl region resonance, are listed in Table III. As shown in Table III, the mmmm pentad content of the isotactic fraction increased with increasing polymerization temperature, although the proportions of the isotactic fraction decreased by increasing the polymerization temperature. On the other hand, the rrrr pentad decreased with increasing temperature. Syndiotactic sequences in PP result from

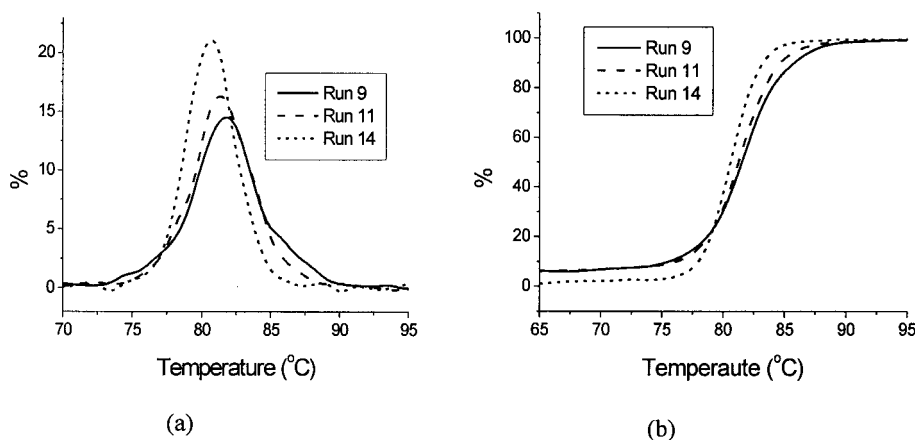
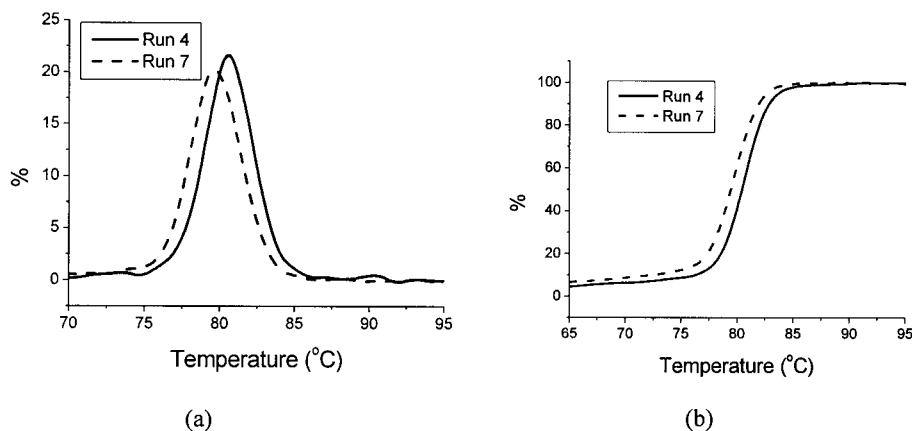


Figure 1 (a) CRYSTAF crystallization temperature profiles. (b) Cumulative fraction as a function of temperature obtained from CRYSTAF for Run 9, Run 11, and Run 14 samples in Table II.



**Figure 2** (a) CRYSTAF crystallization temperature profiles. (b) Cumulative fraction as a function of temperature obtained from CRYSTAF for Run 4 and Run 7 samples in Table I.

chain-end control, and it may be assumed that this became weaker as the temperature increased, resulting in shorter syndiotactic block lengths.

Recently crystallization analysis fractionation (CRYSTAF) has been introduced as a new technique for the analysis of semicrystalline materials and is, similar to TREF,<sup>7</sup> based on the principle of crystallizability.

A commercial CRYSTAF apparatus (model 200, Polymer Char S.A., Valencia, Spain) was used to perform the analysis. Concentrations of 0.1% w/v were used in this investigation, with 30 mg of isotactic polymer samples in 30 mL of 1,2,4-trichlorobenzene solvent. The crystallization rate was 0.1°C/min between 160 and 65°C. Three analyses were performed under the same conditions with each isotactic PP.

The CRYSTAF analyses of samples made with *i*-Bu<sub>3</sub>Al at various temperatures are shown in Figure 1. The CRYSTAF analyses of samples made with Et<sub>3</sub>Al at various temperatures are shown in Figure 2. The CRYSTAF results calculated by its own software are presented in Table IV. As shown in Table IV and Figure 1, the CRYSTAF profiles of Run 9 and Run 11 were nearly identical. This suggested the concentration of *i*-Bu<sub>3</sub>Al had little effect on the crystallization fractions

**TABLE IV**  
Results Obtained from CRYSTAF<sup>a</sup>

Sample	$T_w$ (°C)	$R$	Crystallization fraction (%)		Ratio (Hi:Mi)
			Mi <75°C	Hi ≥75°C	
Run 9	81.3	0.36	9.2	90.8	9.9
Run 11	80.8	0.22	8.6	91.4	10.6
Run 14	80.5	0.14	3.5	96.5	27.6
Run 4	80.1	0.23	8.8	91.2	10.4
Run 7	78.7	0.28	12.9	87.1	6.8

<sup>a</sup> Weight-average temperature:  $T_w = \sum c_i T_i / \sum c_i$ ; number-average temperature:  $T_n = \sum c_i / \sum (c_i / T_i)$ ; dispersion parameters:  $R = 100 \times (T_w / T_n - 1)$ .

of PP at 70°C. When the polymerization temperature was increasing, the crystallization fractions were significantly changed. The fractions of crystallization temperature > 75°C are considered as a highly isotactic fraction and the fractions of crystallization temperature < 75°C as a isotactoid fraction. When the polymerization temperature increased from 70°C (Run 9) to 120°C (Run 14), the highly isotactic fraction increased from 90.8 to 96.5%, which was opposite to the isotactoid fraction from 9.2 to 3.5%. The dispersion parameter ( $R$ ) decreased with increasing polymerization temperature. It showed the higher polymerization temperature led to a narrow dispersion of crystallization fractions.

MgCl<sub>2</sub>-supported catalyst contains multiactive species. Busico et al.<sup>8,9</sup> proposed a three-site model. According to this model, PP produced with MgCl<sub>2</sub>-supported catalysts constitutes three different types of stereosequences: highly isotactic, moderately isotactic (isotactoid), and syndiotactic. It suggested that a stable donor coordination in the vicinity of active species gave rise to higher stereoregularity in the polymer chain than a labile donor coordination.

On the one hand, when the polymerization temperature increased from 70 to 120°C, the proportion of heptane-soluble polymer increased from 3.3 to 22%, which implied that diether(BMMF) in the catalyst was progressively lost as the temperature increased. Thus the isotactoid and syndiotactic species increased. On the other hand, the mmmm content of heptane-insoluble increased with increasing temperature. The ratio of highly isotactic fraction to isotactoid fraction increased from 9.9 to 27.6 as the polymerization temperature increased from 70 to 120°C. Thus an increase in stereoregularity of the fraction of heptane-insoluble results from increasing with a proportion of the fraction of higher stereoregularity, thus implying that the fraction of polymer containing relatively high propor-

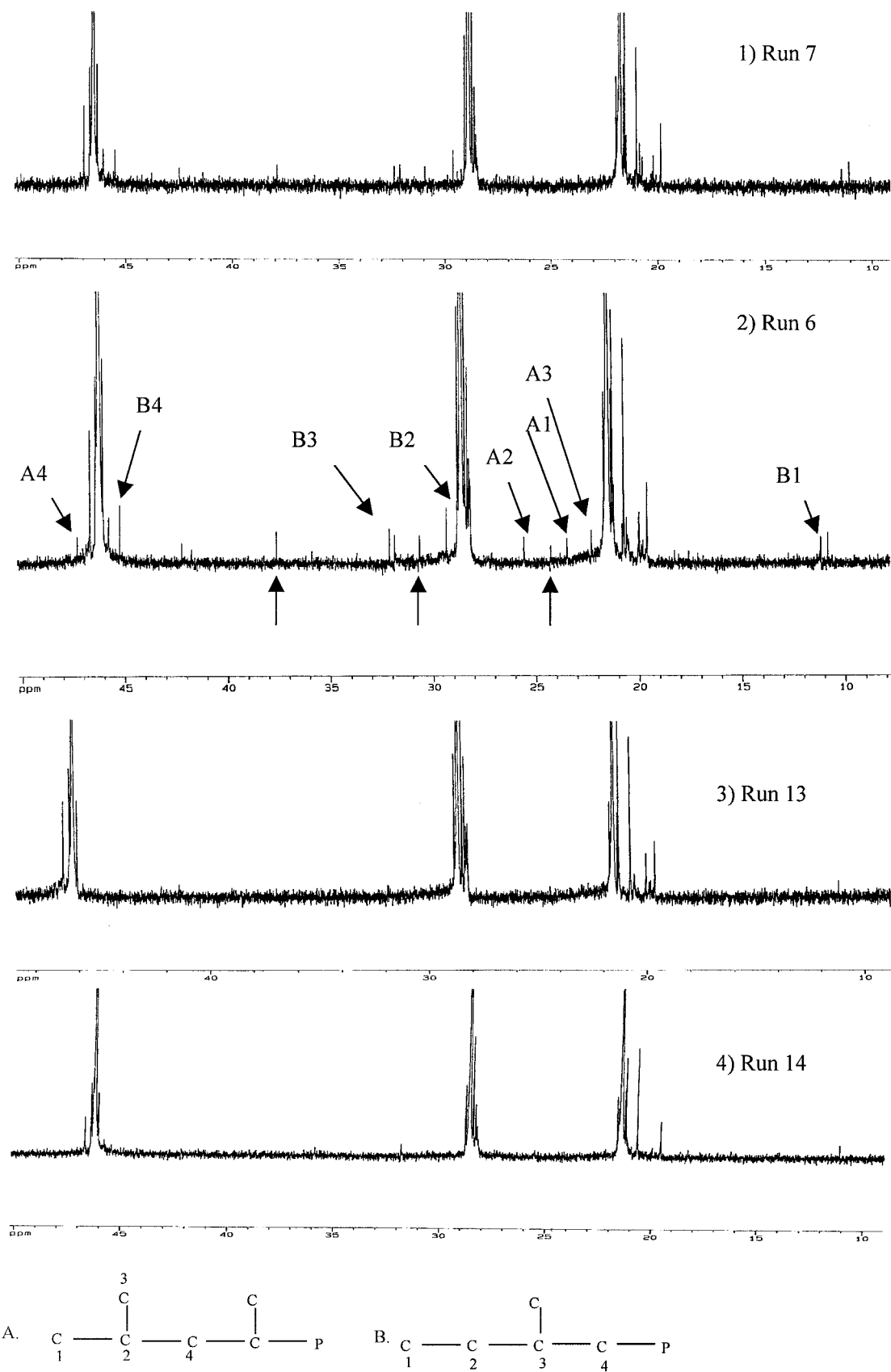


Figure 3  $^{13}\text{C}$ -NMR spectra of the PPs: (1) Run 7, (2) Run 6, (3) Run 13, and (4) Run 14.

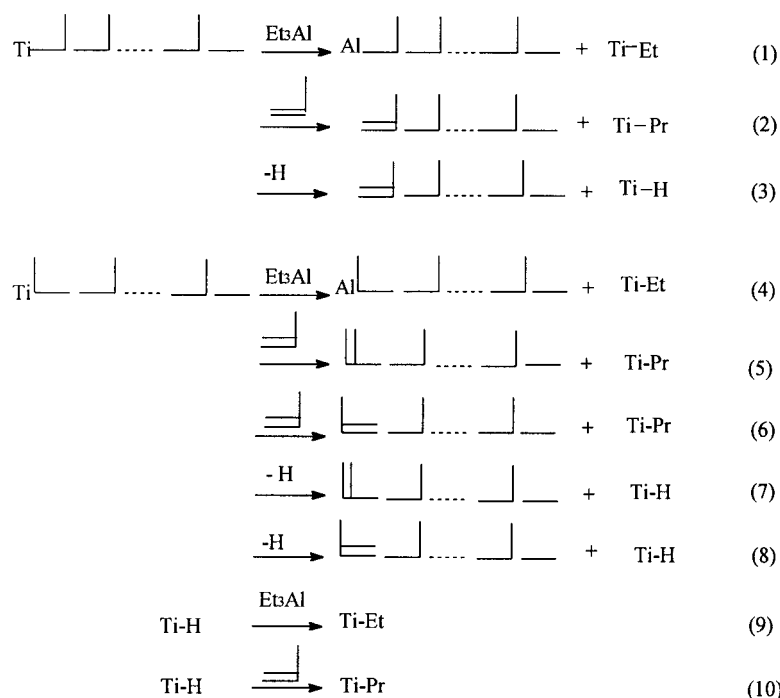


Figure 4 Schemes of all the possible formation reactions of chain ends without hydrogen.<sup>14</sup>

tions of defective isotactic (isotactoid) sequences greatly decreased at high polymerization temperature.

The isotactic PPs obtained with  $\text{Et}_3\text{Al}$  and  $i\text{-Bu}_3\text{Al}$  at  $120^\circ\text{C}$  had nearly identical mmmm pentad content. As shown in Tables I and II, however, the isotactic PP obtained with  $\text{Et}_3\text{Al}$  at  $120^\circ\text{C}$  (Run 7) exhibited a lower melting temperature compared with that of the isotactic PP obtained with  $i\text{-Bu}_3\text{Al}$  (Run 14). The melting temperature ( $T_m$ ) is related to the lamellar thickness, which suggested that through the same cooling process the isotactic PP obtained with  $\text{Et}_3\text{Al}$  gave a thinner crystal than that with  $i\text{-Bu}_3\text{Al}$ . In the polymerization with  $\text{Et}_3\text{Al}$ , as shown in Table IV, the weight-average temperature ( $T_w$ ) obtained at  $120^\circ\text{C}$  (Run 7) was lower than that at  $70^\circ\text{C}$  (Run 4). Moreover, it is interesting that in the polymerization with  $\text{Et}_3\text{Al}$  the ratio of the highly isotactic fraction to isotactoid fraction decreased with increasing polymerization temperature. Such a significant difference of these results between  $\text{Et}_3\text{Al}$  and  $i\text{-Bu}_3\text{Al}$  cannot be explained by a difference in the molecular weight only. Accordingly, these results confirm that the microstructure of PP obtained with  $\text{Et}_3\text{Al}$  at  $120^\circ\text{C}$  was different from that obtained with  $i\text{-Bu}_3\text{Al}$ . Soga et al.<sup>10</sup> and Deng et al.<sup>11</sup> both reported that the low melting points obtained with some metallocene catalysts, even at high pentad isotacticities, were caused by 3,1-misinsertions or 2,1-misinsertions.

The  $^{13}\text{C}$ -NMR spectra of the PPs obtained with  $i\text{-Bu}_3\text{Al}$  and  $\text{Et}_3\text{Al}$  at high polymerization temperature together with the assignments of the peaks are shown

in Figure 3. The top portion of Figure 3 shows the  $^{13}\text{C}$ -NMR spectrum of Run 7; the middle shows the  $^{13}\text{C}$ -NMR spectra of Run 6 and Run 13; and the bottom shows the  $^{13}\text{C}$ -NMR spectrum of Run 14.

Compared with the  $^{13}\text{C}$ -NMR spectra of Run 13 and Run 14, the spectrum of Run 6 obtained with  $\text{Et}_3\text{Al}$  shows a number of small irregular peaks at 37.6, 30.7, and 24.3 ppm and the spectrum of Run 7 shows peaks at 37.6 and 30.7 ppm. Soga et al.<sup>10</sup> reported the peaks (37.5, 30.9, and 27.6 ppm) were assigned to 3,1-misinsertion. Kojoh et al.<sup>1</sup> believed the peaks at 37.6 and 24.3 ppm arose out of copolymerization with ethylene and at high temperature ethylene was decomposed from  $\text{Et}_3\text{Al}$ . Because these results did not appear in the polymerization with  $i\text{-Bu}_3\text{Al}$ , the higher polymerization temperature is not the only reason for these. We think the explanation put forth by Kojoh et al.<sup>1</sup> may be reasonable. The peak at 24.3 ppm did not appear in Run 7 because of the low concentration of  $\text{Et}_3\text{Al}$ .

Because the molecular weights of the PPs obtained at  $100^\circ\text{C}$  (Run 6) and at  $120^\circ\text{C}$  (Run 7) were low enough, the terminal groups of these PPs were also found in  $^{13}\text{C}$ -NMR spectra, as shown in Figure 3. The carbon peaks of terminal groups were assigned according to Kojoh et al.,<sup>1</sup> Cheng and Smith,<sup>12</sup> and Grassi et al.<sup>13</sup> As shown in Figure 3, the terminal groups of PP obtained at  $100^\circ\text{C}$  with  $\text{Et}_3\text{Al}$  were ethyl and isobutyl groups. However, the terminal groups of PP obtained at  $120^\circ\text{C}$  with  $\text{Et}_3\text{Al}$  were ethyl groups. A small peak at 111.2 ppm was found in both Run 6 and

Run 7, and thus the 2-propylene terminal groups existed in Run 6 and Run 7.<sup>12</sup>

All the possible terminal groups formed by chain-transfer reaction without hydrogen addition are shown in eqs. (1)–(10) in Figure 4.<sup>14</sup> The terminal groups of *n*-Pr were not detected either at 100°C (Run 6) or at 120°C (Run 7); thus the chain transfer of the propagating chain to monomer may be extremely low. *n*-Bu as the terminal groups cannot be found, and thus eq. (4) can be denied. The PP having *i*-Bu as the terminal groups is formed only through the reaction by Et<sub>3</sub>Al in accordance with eq. (1). The terminal groups of *i*-Bu were not detected at 120°C (Run 7). The 2-propylene terminal groups were found only as unsaturated structures. These results suggested that at 120°C the chain-transfer reaction by  $\beta$ -H abstraction [eq. (3)] was the main chain-transfer reaction.

### CONCLUSIONS

1. When *i*-Bu<sub>3</sub>Al was used as cocatalyst in propylene polymerization using the heterogeneous TiCl<sub>4</sub>/MgCl<sub>2</sub>/diether(BMMF) catalyst, the activity at 100°C was as high as that at 70°C.
2. When Et<sub>3</sub>Al was used as cocatalyst at a low concentration, the molecular weight obtained at 100°C was higher than that at 70°C.
3. With increasing polymerization temperature the concentrations of [mmmm] of heptane-insoluble polypropylene fraction increased, which resulted from the fractions of different crystallization tem-

peratures that changed according to various polymerization temperatures. Investigation of the effects on the heptane-soluble fraction is in progress.

4. At 120°C the chain-transfer reaction by  $\beta$ -H abstraction was the main chain-transfer reaction.

### References

1. Kojoh, S.; Kioka, M.; Kashiwa, N. *Eur Polym J* 1999, 35, 751.
2. Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerizations*; Chemical Industrial Press: Beijing, 1986; pp. 178–181.
3. Mao, B.; Yang, A.; Zheng, Y.; Yang, J.; Li, Z. U.S. Pat. 4,861,847, 1989.
4. Xu, D.; Liu, Z.; Zhao, J.; Han, S.; Hu, Y. *Macromol Rapid Commun* 2000, 21, 1046.
5. Chadwick, J. C.; Morini, G.; Balbontin, G.; Sudmeijer, O. *Macromol Chem Phys* 1998, 199, 1873.
6. Chadwick, J. C.; Morini, G.; Balbontin, G.; Camurati, I.; Heere, J. J. R.; Mingozzi, I.; Testoni, F. *Macromol Chem Phys* 2001, 202, 1995.
7. Monbabal, B. *J Appl Polym Sci* 1994, 52, 491.
8. Busico, V.; Cipullo, R.; Talarico, G. *Macromolecules* 1997, 30, 4786.
9. Busico, V.; Cipullo, R.; Monaco, G.; Talarico, G.; Vacatello, M.; Chadwick, J. C.; Segre, A. L.; Sudmeijer, O. *Macromolecules* 1999, 32, 4173.
10. Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol Chem Rapid Commun* 1987, 8305.
11. Deng, H.; Winkelbach, H.; Taeji, K.; Kaminsky, W.; Soga, K. *Macromolecules* 1996, 29, 6371.
12. Cheng, H. N.; Smith, D. A. *Macromolecules* 1986, 19, 2065.
13. Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* 1988, 21, 617.
14. Kojoh, S.; Kioka, M.; Kashiwa, N.; Itoh, M.; Mizuno, A. *Polymer* 1995, 36, 5015.