

# Control of Molecular Weight Distribution for Polypropylene Obtained by a Commercial Ziegler–Natta Catalyst: Effect of a Cocatalyst and Hydrogen

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**ABSTRACT:** The polymerization of propylene was carried out with an MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst (with diisobutyl phthalate as an internal donor) in the absence and presence of hydrogen (H<sub>2</sub>) as a chain-transfer agent. Different structures of alkylaluminum were used as cocatalysts. The effects of the alkyl group size of the cocatalyst, H<sub>2</sub> feed, and feed time on the propylene polymerization behaviors were investigated. The catalyst activity significantly decreased with increasing alkyl group size in the cocatalyst. The molecular weight and polydispersity index (PDI) increased with increasing alkyl group size. With the introduction of H<sub>2</sub>, the catalyst activity increased signifi-

cantly, whereas the molecular weight and PDI of polypropylene (PP) decreased. Additionally, the effect of the polymerization time in the presence of H<sub>2</sub> on the propylene polymerization was studied. The molecular weight distribution curve was bimodal at short polymerization times in the presence of H<sub>2</sub>, and we could control the molecular weight distribution of PP by changing the polymerization time in the presence of H<sub>2</sub>. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 101–108, 2011

**Key words:** molecular weight distribution/molar; polyolefins; Ziegler–Natta polymerization

## INTRODUCTION

Polyolefins were produced worldwide in a very large volume, about 120 × 10<sup>6</sup> metric tons in 2006, which corresponded to over 50% of the total production of all plastic materials.<sup>1</sup> Propylene polymers and copolymers accounted for about 35% of the total polyolefin production, and more than 90% of the world production of polypropylene (PP) was produced by Ziegler–Natta catalysts.<sup>1,2</sup>

In propylene polymerization by typical MgCl<sub>2</sub>-supported Ti-based catalysts, alkylaluminum (especially trialkylaluminum) is the most commonly used cocatalyst.<sup>3</sup> It was reported by Collina et al.<sup>4</sup> that the catalyst activity and polymer isotacticity were influenced by the structure of cocatalyst, whereas Gupta and Ravindranathan<sup>5</sup> showed that isotacticity was less affected by that kind of cocatalyst. A great variety of alkylaluminums, including triethylaluminum (TEA), tri-*i*-butylaluminum (TiBA), tri-*n*-hexylaluminum (THA), tri-*n*-octylaluminum (TOA), and diethylaluminum chloride (DEAC),<sup>6–9</sup> have been used as cocatalysts to activate olefin polymerization.

On the other hand, hydrogen (H<sub>2</sub>) is known to be the most efficient industrial regulator of the molecular weight of propylene polymerization as a chain-transfer agent.<sup>10</sup> The use of H<sub>2</sub> as a molecular weight regulator is based on the hydrogenolysis of metal to polymer bonds, and the rate of chain transfer to H<sub>2</sub> is substantially higher than the rate of chain transfer to olefin or alkyl aluminum.<sup>10,11</sup> Most of the results reported so far have shown that the molecular weight of PP decreases proportionally to the square root of the partial pressure of H<sub>2</sub>; this suggests that H<sub>2</sub> might act as a chain-transfer agent solely in the atomic state after dissociation on the catalysts.<sup>10,12</sup>

It is well known that the molecular weight distribution has a significant effect on the processability and end-use properties of PP polymers.<sup>13,14</sup> Therefore, it is necessary to control the molecular weight distribution of PP to produce various grades suitable for the many end-use applications of PP. Several methods for controlling the molecular weight and molecular weight distribution of polymers are available, such as the physical blending of polymers with different average molecular weights,<sup>15</sup> the cascade reactor process,<sup>16</sup> and the mixing or hybridization of different catalysts.<sup>17</sup> However, these methods more or less have some defects, such as gelation, high cost, and complex manipulation.<sup>15</sup> Therefore, it is necessary to seek a single polymerization system to control the molecular weight distribution of PP.

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The aim of this study was to examine the effects of a cocatalyst and H<sub>2</sub> on the catalyst activity, isospecificity, molecular weight, and molecular weight distribution of PP with an MgCl<sub>2</sub>-supported Ti-based catalyst system. In addition, the effect of the polymerization time in the presence of H<sub>2</sub> on the molecular weight and molecular weight distribution of PP was investigated.

## EXPERIMENTAL

### Materials

The MgCl<sub>2</sub>-supported Ti-based catalysts (catalyst A, diisobutyl phthalate, 2.0 wt % Ti, and catalyst B, diisobutyl phthalate, 2.4 wt % Ti) and external donor (dicyclopentylmethoxysilane) were provided by Samsung Total Petrochemicals Co. (Daesan, Korea). TEA, TiBA, and DEAC were purchased from Tosoh Akzo Corp. (Yamaguchi, Japan). THA and TOA were purchased from Acros (Geel, Belgium). *n*-Hexane was distilled from sodium/benzophenone under nitrogen before use.

### Polymerization procedure

The polymerization was carried out in a 300-mL glass reactor equipped with a magnetic stirring bar. The reactor was back-filled three times with nitrogen and charged with the required amount of *n*-hexane. At the stipulated temperature of 40°C, the reaction solution was vigorously stirred under 1 atm of propylene for the desired period of time, after which the cocatalyst was added to the reactor. After the cocatalyst was added, the external donor and a catalyst solution were injected, and then, the polymerization was started with a continuous feed of propylene in the absence and presence of H<sub>2</sub>. The feed ratio of propylene and H<sub>2</sub> was controlled by a flow control meter, and the polymerization temperature was controlled with a water bath. After 2 h, the polymerization was terminated by the addition of a 10% HCl-methanol solution, and then, the mixture was poured into 500 mL of methanol to precipitate the polymer. The precipitate was then dried *in vacuo* at 60°C to a constant weight. The polymer was fractionated by extraction with boiling *n*-heptane for 8 h to determine the isotactic index (II).

With regard to the effect of the polymerization time in the system with H<sub>2</sub>, the same polymerization procedure was applied. The polymerization was started with a continuous feed of propylene in the absence of H<sub>2</sub>. At fixed times (0, 15, 30, 45, 60, 75, 90, and 105 min) after the polymerization was started, a continuous flow of H<sub>2</sub> gas was introduced, and the H<sub>2</sub> feed ratio ( $V_H : V_P = 0.25$ ) was controlled by a flow meter, where  $V_H$  and  $V_P$  are the volume

of H<sub>2</sub> and propylene, respectively. The total polymerization time was 2 h.

### Polymer characterization

The polymer product was fractionated by extraction with boiling *n*-heptane for 8 h to determine II, and the II values reported for each samples were the weight percentages of *n*-heptane insoluble polymer.

The melting temperature ( $T_m$ ) was determined by differential scanning calorimetry (DSC; DuPont TA 4000, TA Instruments, USA) at a heating rate of 10°C/min. The materials were cooled from the melt (200°C) to 30°C at a rate of 10°C/min, and  $T_m$  and the heat of fusion were determined in the second scan. The crystallinity ( $X_c$ ) was calculated assuming  $\Delta H_{PP} = 209$  J/g.<sup>18,19</sup>

The molecular weight and polydispersity index (PDI) of the *n*-heptane-insoluble PP fractions were determined by gel permeation chromatography (GPC) with a 1,2,4-trichlorobenzene solution at 135°C with a PL-220 instrument (Polymer Laboratories, UK) equipped with a refractive-index detector.

### Calculation of theoretical PDI

Two hypothetical polymers (polymers A and B) with different molecular weights were used to describe the calculation process. The calculation of theoretical PDI was done (1) to unify the total amount of polymer fraction in the GPC curves [Fig. 1(a); Area<sub>A</sub> = Area<sub>B</sub>], (2) to determine the related amounts of fractions A and B to the combined GPC curve (e.g., the yield of polymer A was 2 g and the polymer yield of B was 1 g when the polymerization system was a mixture of polymers A and B at a 1 : 1 feed ratio; in theory, the obtained polymer would contain 1 g of polymer A and 0.5 g of polymer B), and (3) to combine the curves of polymers A and B according to the following process:

$$y_1 = y_A \times A_A / (A_A + A_B) \quad (1)$$

$$y_2 = y_B \times A_B / (A_A + A_B) \quad (2)$$

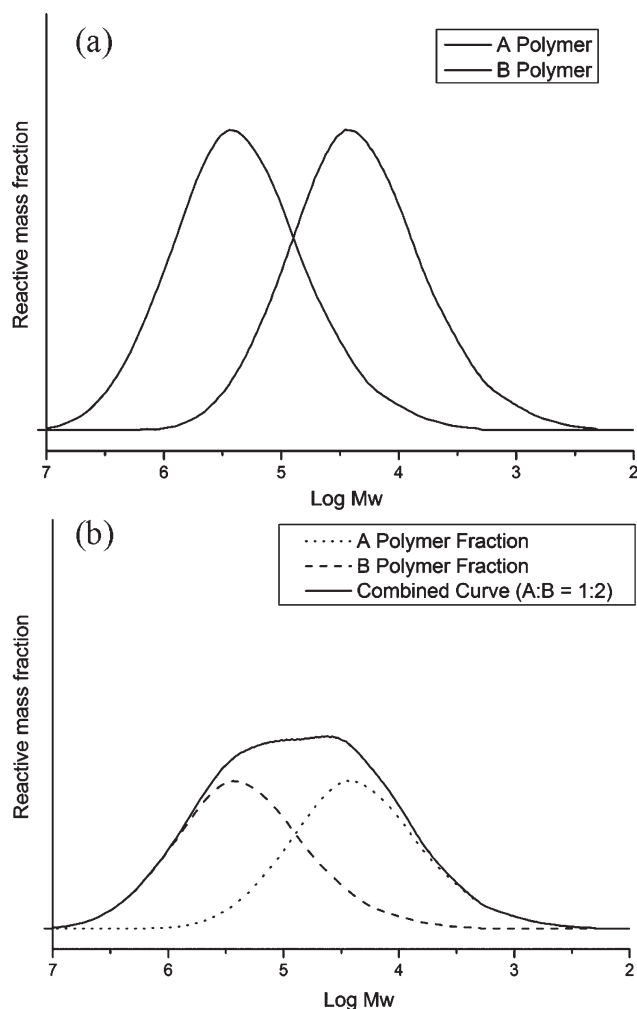
$$y_{\text{Combined}} = y_1 + y_2 \quad (3)$$

where  $y_1$  and  $y_2$  are the fraction of polymer A and B,  $y_A$  and  $y_B$  are the  $y$  axes of the GPC curves obtained from polymers A and B, respectively [Fig. 1(a)].  $A_A$  and  $A_B$  are the related amounts of polymers A and B, respectively.  $y_{\text{Combined}}$  is the  $y$  axis of the theoretical GPC curve. The combined GPC curve is shown in Figure 1(b). The theoretical PDI was calculated from the combined GPC curve.

## RESULTS AND DISCUSSION

### Effect of the cocatalyst

The polymerization of propylene was carried out with an MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst in the



**Figure 1** (a) Hypothetical GPC curves of polymers A and B and (b) theoretical curve of the polymer mixture (A/B = 1 : 1).

absence and presence of  $H_2$  as a chain-transfer agent. The propylene pressure was kept constant throughout the polymerization through the use of a bubbler, the feed ratio of propylene and  $H_2$  was controlled by a flow meter. The polymerization behavior was examined with various alkyl aluminums (TEA, TiBA, THA, TOA, and DEAC) and their mixtures. The experimental results are given in Table I.

As shown in Table I, the catalyst activity decreased with increasing alkyl group size in the cocatalyst. The results corresponded to the bulky alkyl group in the cocatalyst, which prevented the aluminum from coming closer to the titanium for active species formation.<sup>5</sup> Mori et al.<sup>8</sup> reported that the active site concentration decreased drastically with increasing the bulkiness of the alkyl group of trialkylaluminum. The reason for the low active-site concentration of alkylaluminum with bulky alkyl groups was attributed to the difficulty of the reaction with titanium species. The activity of the cata-

lyst with different cocatalysts decreased in the following order: TEA > TiBA > THA  $\geq$  TOA  $\geq$  DEAC. The lower activity of DEAC as a cocatalyst was ascribed to the fewer titanium species activated for DEAC.<sup>8</sup> With regard to the cocatalyst mixture system, the catalyst activity increased with the introduction of DEAC as the second cocatalyst (except TEA). The reason was the formation of a complex between the trialkylaluminum and DEAC and/or the formation of an Al–Al bond and an alkyl chloride.<sup>20</sup> The presumed reaction is shown in Figure 2.

Also, the catalyst activity increased with the introduction of  $H_2$ . The increased catalyst activity was ascribed to the change in the oxidation state of the active centers. In the presence of  $H_2$ ,  $[Ti^{2+}]$  decreased, and  $[Ti^{3+}]$  increased.<sup>21</sup> According to Soga et al.<sup>22</sup>  $[Ti^{3+}]$  can be polymerized with both ethylene and propylene, whereas  $[Ti^{2+}]$  is only active in ethylene polymerization. The highest value of catalyst activity was obtained with TEA as the cocatalyst in the presence of  $H_2$ .

As shown in Table I, II roughly decreased with increasing alkyl group size of the cocatalyst. Yang and Hsu<sup>23</sup> suggested that the effectiveness of removing the internal donor by alkylaluminum may diminish as the alkyl group became bulky and that the alkylation of the Ti species to form isotactic sites may be adversely affected by steric factors around the isotactic sites. The maximum II value (98.8 wt %) was attained when TEA was used as the cocatalyst in the absence of  $H_2$ . However, the effect of  $H_2$  on the II value of the obtained PP was insignificant, and the same phenomenon was observed by Forte and Coutinho.<sup>24</sup> An II value of higher than 95 wt % was obtained in the whole range of this study.

The  $T_m$  value of PP was less changed with increasing alkyl group size of the cocatalyst, whereas  $X_c$  slightly decreased with increasing alkyl group size. The selected DSC curves of PP are shown in Figure 3; only one sharp crystalline peak was observed.

With respect to the decreased  $X_c$ , the reason have presumably been that the higher molecular weight of PP obtained by the bulky alkyl group cocatalyst led to the formation of more irregular PP spherulites.<sup>25</sup> In addition,  $T_m$  and  $X_c$  of PP improved significantly with the introduction of  $H_2$ . The increased  $T_m$  and  $X_c$  may have corresponded to the shorter chain of PP obtained in the presence of  $H_2$ , whereas the shorter chain PP led to a decrease in the nature and frequency of the steric errors and the formation of more regular PP spherulites.  $T_m$  of PP increased from 159.6 to 166.8°C, and  $X_c$  was in the range 30.3–50.4%.

The molecular weight distribution curves of the *n*-heptane insoluble fractions of the samples obtained with the  $MgCl_2$ -supported  $TiCl_4$  catalysts activated

TABLE I  
Effect of the Cocatalyst and H<sub>2</sub> on Propylene Polymerization<sup>a</sup>

Cocatalyst	V <sub>H</sub> /V <sub>P</sub>	Activity <sup>b</sup>	II (wt %)	T <sub>m</sub> (°C)	X <sub>c</sub> (%)	M <sub>w</sub> <sup>c</sup>	PDI	PDI <sup>d</sup>
TEA	—	4.3	98.8	159.1	41.3	61.0	6.5	—
	0.25	6.8	97.9	165.7	43.2	11.5	5.7	—
TiBA	—	1.0	97.8	160.8	40.6	76.1	7.0	—
	0.25	2.9	96.8	166.7	43.1	20.7	6.0	—
THA	—	0.6	97.1	161.4	35.7	77.8	7.8	—
	0.25	0.9	97.2	167.1	37.7	19.5	7.0	—
TOA	—	0.7	97.2	161.1	38.2	96.8	9.4	—
	0.25	0.9	96.8	167.7	40.8	23.8	6.8	—
DEAC	—	0.4	96.8	159.5	36.8	45.5	7.6	—
	0.25	0.9	95.6	165.1	37.3	12.8	5.9	—
TEA + TiBA <sup>e</sup>	—	1.6	96.2	161.2	37.9	62.8	6.9	6.7
	0.25	2.9	97.2	164.0	40.7	17.7	6.4	6.2
TEA + THA <sup>e</sup>	—	2.2	96.6	160.4	39.6	66.7	7.6	6.7
	0.25	3.7	96.4	166.7	42.9	15.6	5.6	5.9
TEA + TOA <sup>e</sup>	—	3.1	96.8	159.8	39.8	69.9	8.1	7.0
	0.25	4.9	95.8	166.1	42.8	16.1	5.8	6.1
TEA + DEAC <sup>e</sup>	—	2.8	98.3	161.3	40.6	54.0	6.9	6.7
	0.25	3.1	96.4	163.9	44.6	7.1	6.2	5.7
TiBA + THA <sup>e</sup>	—	0.8	96.6	159.9	39.2	76.8	7.9	7.3
	0.25	1.2	98.2	167.3	40.5	22.7	6.5	6.2
TiBA + TOA <sup>e</sup>	—	0.9	98.2	158.7	40.6	80.5	8.4	8.0
	0.25	1.4	97.6	166.5	42.2	23.0	6.6	6.1
TiBA + DEAC <sup>e</sup>	—	1.9	96.4	160.4	39.5	64.0	8.0	7.6
	0.25	2.7	95.7	164.5	44.1	10.6	6.9	6.2
THA + TOA <sup>e</sup>	—	0.6	95.8	162.4	40.6	87.3	8.9	8.7
	0.25	0.9	96.7	167.9	42.7	24.4	6.8	6.9
THA + DEAC <sup>e</sup>	—	0.9	97.6	159.1	38.7	55.1	8.5	8.2
	0.25	1.4	97.3	164.7	40.9	13.8	6.6	6.6
TOA + DEAC <sup>e</sup>	—	1.3	96.8	160.7	41.6	72.4	9.5	9.6
	0.25	2.7	95.4	166.3	45.0	11.5	6.7	6.9

<sup>a</sup> Polymerization conditions: catalyst A, [Ti] = 1.2 × 10<sup>-4</sup> mol/L, [Al]/[Ti] = 400, [external donor]/[Al] = 0.1, atmospheric pressure, 40°C, 2 h.

<sup>b</sup> Activity: kg of polymer (g of Ti)<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup> × 10<sup>-4</sup> g/mol.

<sup>d</sup> Theoretical.

<sup>e</sup> Cocatalyst 1/cocatalyst 2 = 1 : 1 (mol/mol).

by different alkylaluminum cocatalysts are shown in Figure 4.

The molecular weight distribution curves of PP obtained by different alkylaluminum cocatalysts in

the absence and presence of H<sub>2</sub> were symmetrical. The molecular weight of the obtained PP increased with increasing alkyl group size of the cocatalyst. The results were ascribed to the efficiency of

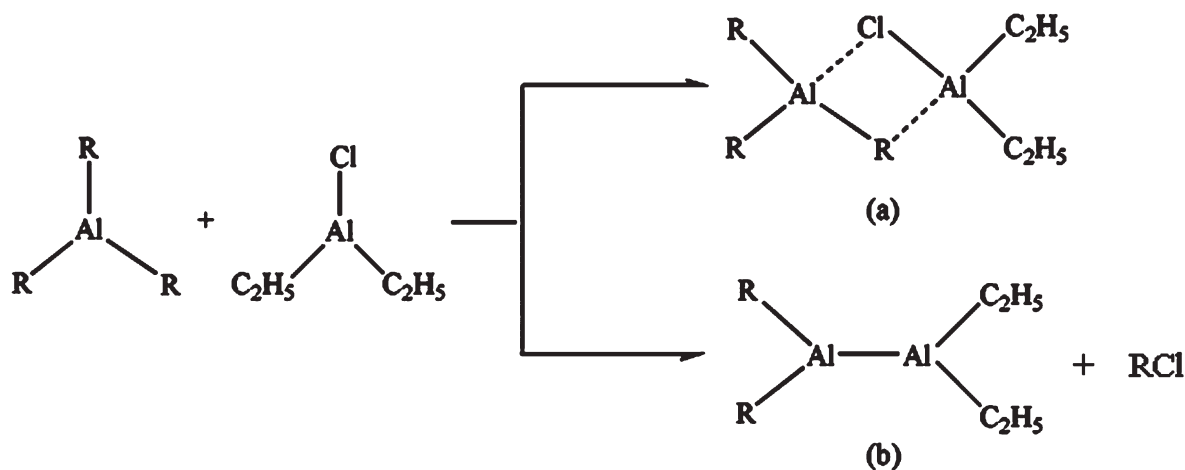
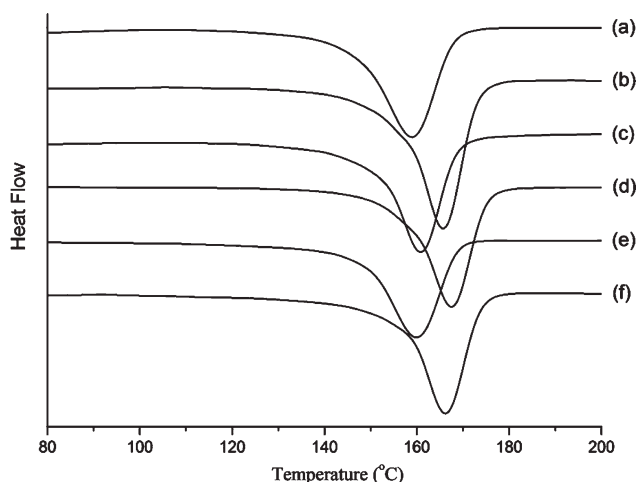


Figure 2 Presumed reaction between trialkylaluminum and DEAC (R = alkyl).



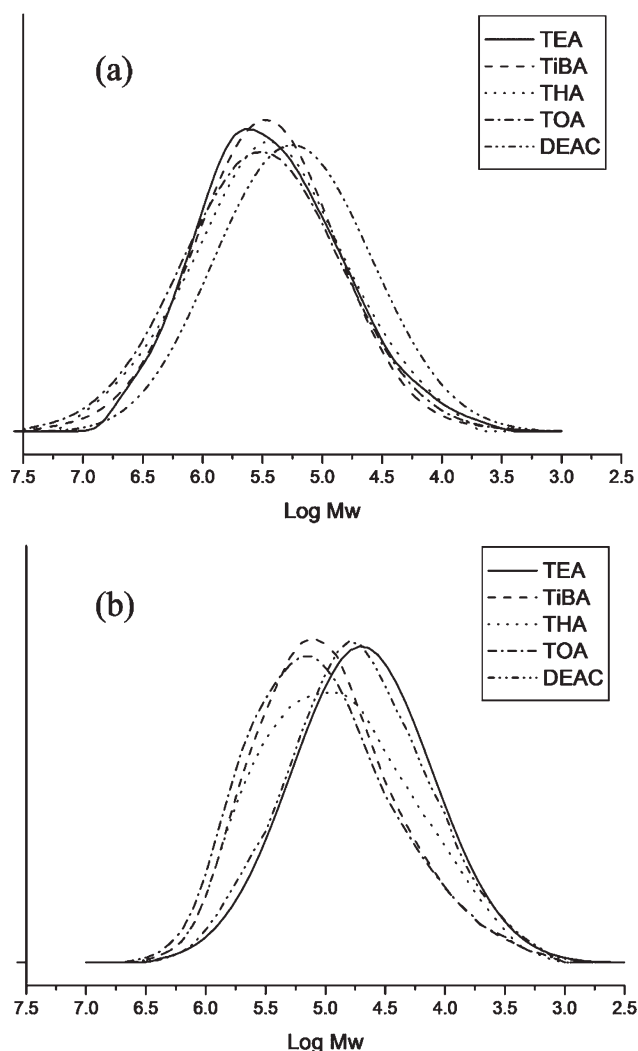


**Figure 3** Selected DSC curves of PP: (a) TEA (no H<sub>2</sub>), (b) TEA ( $V_H/V_P = 0.25$ ), (c) TOA (no H<sub>2</sub>), (d) TOA ( $V_H/V_P = 0.25$ ), (e) TEA + TOA (no H<sub>2</sub>), and (f) TEA + TOA ( $V_H/V_P = 0.25$ ).

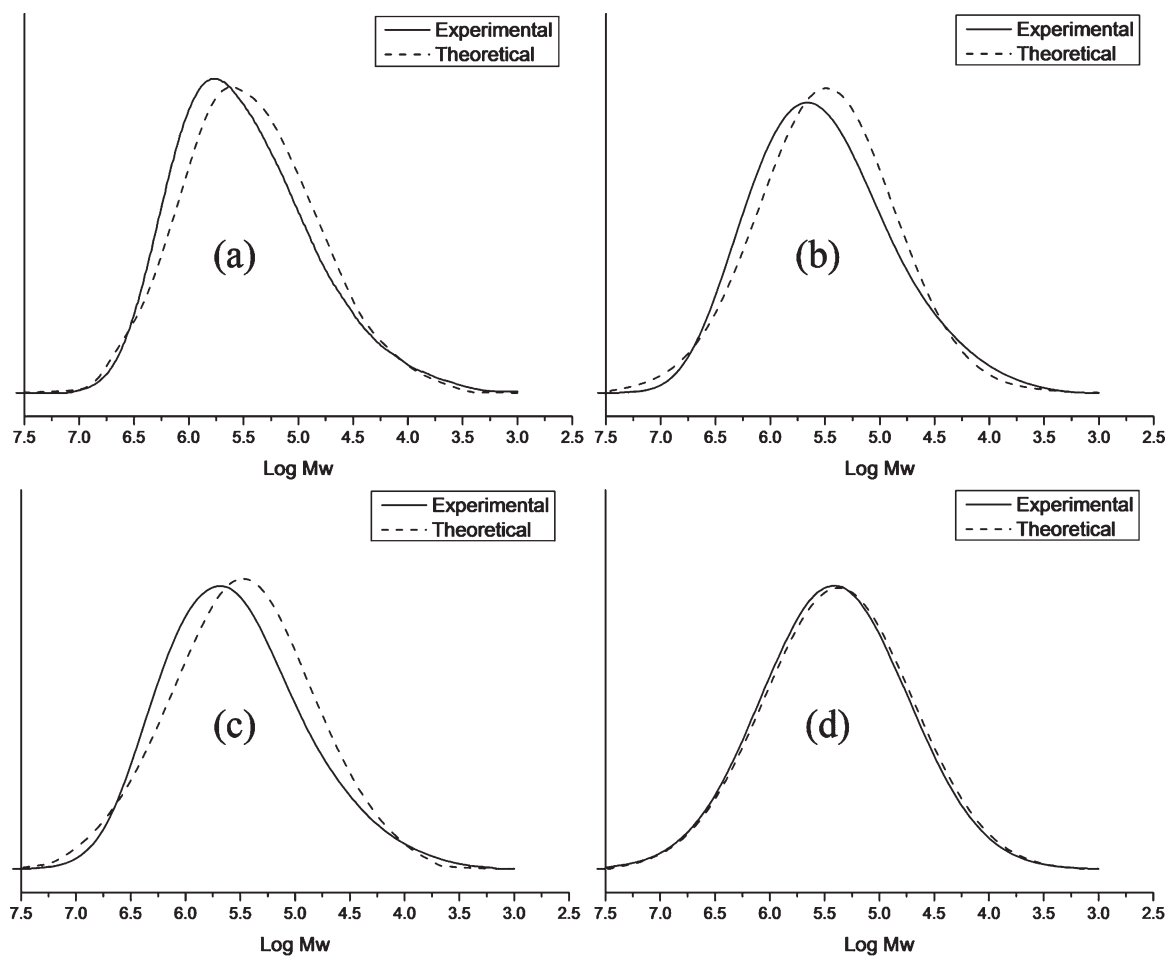
alkylaluminum as a chain-transfer reagent, which was dependent on the steric hindrance of the alkyl group in the cocatalyst.<sup>26</sup> Namely, the chain-transfer reagent with the larger alkyl group size was less effective because of its alkyl group's bulkiness. Also, the molecular weight of PP decreased with the introduction of H<sub>2</sub>. The decreased molecular weight could have been due to the strong chain-transfer reaction of H<sub>2</sub>; the same results have been reported by many researchers.<sup>10–12</sup> The highest molecular weight was obtained with TOA as the cocatalyst in the absence of H<sub>2</sub>. The weight-average molecular weights ( $M_w$ 's) of PP were in the range  $45.5 \times 10^{-4}$  to  $96.8 \times 10^{-4}$  g/mol for polymerization in the system without H<sub>2</sub> and  $7.1 \times 10^{-4}$  to  $24.4 \times 10^{-4}$  g/mol for polymerization in the system with H<sub>2</sub>. PDI increased with increasing alkyl group size of the cocatalyst. The PDI of PP increased with increasing alkyl size of cocatalysts. It was considered that the number of activated active sites increased with the increasing of alkyl size and/or considerable active sites were destroyed by the small size alkyl group of cocatalysts.<sup>27</sup> PDI decreased with the introduction of H<sub>2</sub>. Soga and Shiono<sup>28</sup> reported that the molecular weight distribution of their obtained PP decreased with increasing H<sub>2</sub> partial pressure also. The reason may have been the decrease in the concentration of the growing chains caused by the chain transfer by H<sub>2</sub>. The effect of the cocatalyst mixture on the PDI value of PP was investigated, and the theoretical PDI value for the cocatalyst mixture system was also calculated. The theoretical PDI values of the cocatalyst mixture system were calculated from the combined molecular weight distribution curve of PP obtained by the two cocatalysts used for the mixture. The ratio of the combined molecular weight

distribution curves was determined by the ratio of the polymer product obtained by polymerization with the two cocatalysts, respectively. The experimental and theoretical molecular weight distribution curves of TOA as the second cocatalyst are shown in Figure 5.

The experimental molecular weight distribution curves were slightly shifted to a higher molecular weight region. The reason may have been that the reaction between the two alkylaluminum cocatalysts led to a decrease in the chain-transfer efficiency of alkylaluminum. In addition, the exchange reaction between different alkylaluminum cocatalysts may have led to the formation of new types of alkylaluminum complexes. The molecular weight distribution of the obtained PP could be controlled in the range from 5.6 to 9.5 by using the different alkylaluminiums and H<sub>2</sub>.



**Figure 4** Molecular weight distribution curves of PP obtained by different alkylaluminum cocatalysts in the (a) absence and (b) presence of H<sub>2</sub>.



**Figure 5** Experimental and theoretical molecular weight distribution curves of TOA as the second cocatalyst: (a) TEA + TOA, (b) TiBA + TOA, (c) THA + TOA, and (d) DEAC + TOA.

### Effect of the polymerization time in the presence of $H_2$

$H_2$  is a commercially applicable chain-transfer agent in olefin polymerization processes over a Ziegler–Natta catalyst. The effect of  $H_2$  on the polymerization of propylene has been reported by many researchers.<sup>10–12</sup> According to the previous section's result, the molecular weight decreased with the introduction of  $H_2$ . To broaden the molecular weight distribution, a two-step polymerization procedure was introduced. The polymerization was carried out with an  $MgCl_2$ -supported  $TiCl_4$  catalyst in the absence of  $H_2$  to produce a higher molecular weight polymer. After a fixed times (0, 15, 30, 45, 60, 75, 90, 105, and 120 min),  $H_2$  was introduced into the polymerization system to yield the lower molecular weight polymer. The polymerization of propylene was carried with catalyst B in conjunction with TEA as a cocatalyst and dicyclopentylidimethoxysilane as an external donor. The effect of the polymerization time in the presence of  $H_2$  on the catalyst activity is given in Table II.

As expected, the catalyst activity increased continually with increasing polymerization time in the presence of  $H_2$ . The II value of PP was less influenced by the polymerization time in the presence of  $H_2$  and remained in the range from 97 to 99 wt %.  $T_m$  and  $X_c$  increased with increasing polymerization time in the presence of  $H_2$ .  $T_m$  of the obtained PP increased from 161.8 to 164.5°C; this corresponded to 0–120 min of polymerization time in the presence of  $H_2$ , and  $X_c$  was in the range from 49.3 to 57.4%.

The increase in polymerization time in the presence of  $H_2$  presented a stronger effect on the PP molecular weight. The molecular weight decreased with increasing polymerization time in the presence of  $H_2$ . The decreased molecular weight of PP could have corresponded to the chain-transfer reaction of  $H_2$ <sup>10–12</sup> The PDI value increased with increasing polymerization time in the presence of  $H_2$  to a maximum value and then decreased with the polymerization time in the presence of  $H_2$ . The maximum PDI value was obtained at a polymerization time of 60 min in the presence of  $H_2$ . In addition, the

TABLE II  
Effect of the Polymerization Time in the Presence of H<sub>2</sub> on the Propylene Polymerization<sup>a</sup>

Polymerization time in the presence of H <sub>2</sub> (min)	Activity <sup>b</sup>	II (wt %)	T <sub>m</sub> (°C)	X <sub>c</sub> (%)	M <sub>w</sub> <sup>c</sup>	PDI	PDI <sup>d</sup>
0	1.7	98.2	162.3	49.3	67.0	8.5	8.5
15	1.7	98.4	162.3	50.6	44.9	10.1	12.6
30	1.8	97.1	162.6	50.5	36.0	11.0	13.3
45	2.6	98.4	161.8	52.3	32.6	11.3	12.7
60	3.1	96.8	163.0	54.9	28.8	11.6	11.6
75	3.8	97.2	164.2	53.7	25.1	11.2	10.3
90	4.0	99.0	162.7	53.5	23.2	9.6	9.0
105	4.9	98.3	163.5	52.6	19.5	8.5	7.7
120	4.7	97.1	164.5	57.4	11.9	6.6	6.6

<sup>a</sup> Polymerization conditions: [Ti] = 1.2 × 10<sup>-4</sup> mol/L, [Al]/[Ti] = 400, [External donor]/[Al] = 0.1, atmospheric pressure, 40°C, 2 h.

<sup>b</sup> Activity: kg of polymer (g of Ti)<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup> × 10<sup>-4</sup> g/mol.

<sup>d</sup> Theoretical.

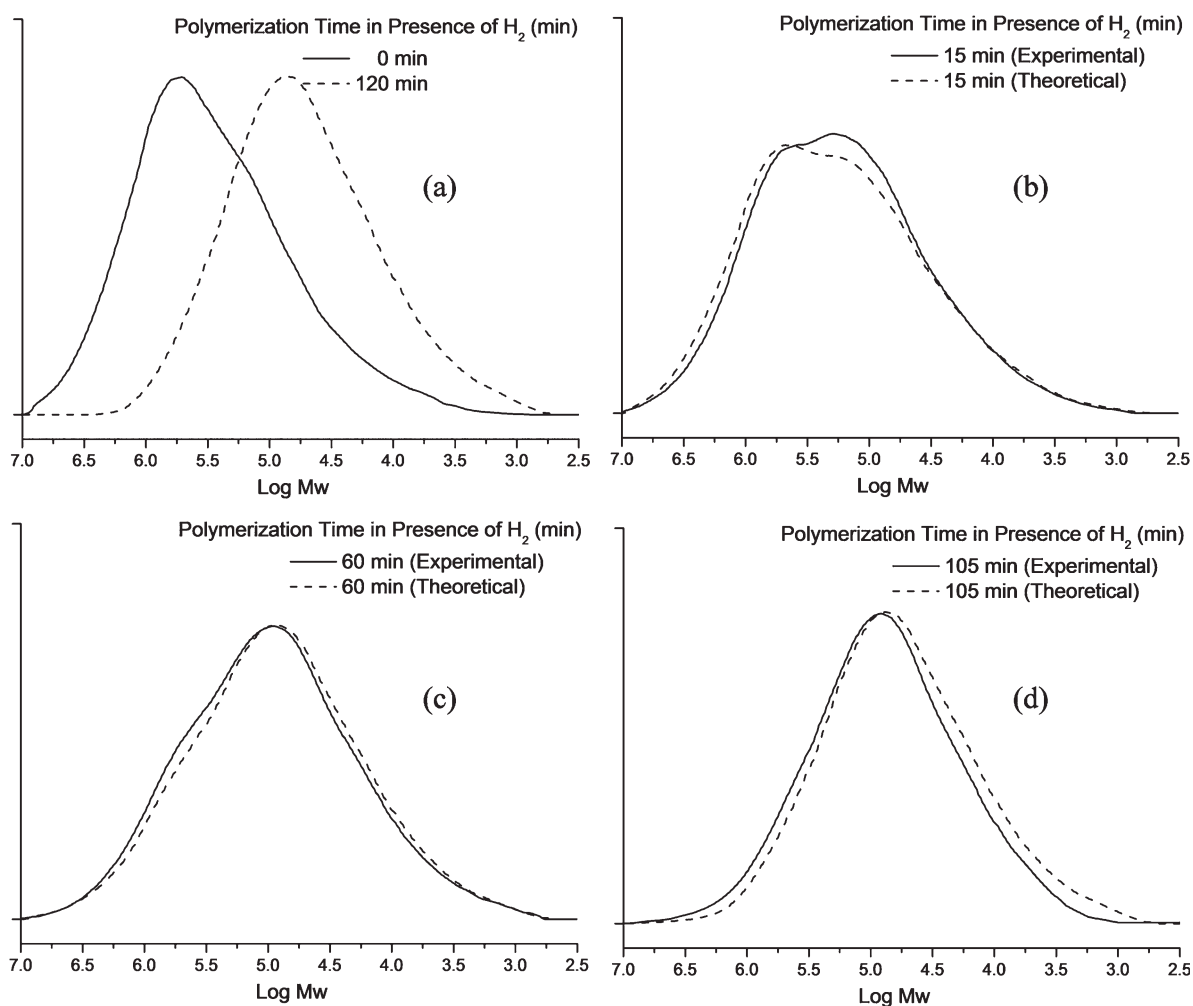


Figure 6 Molecular weight distribution curves of (a) 0, 120, (b) 15, (c) 60, and (d) 105 min of polymerization in the presence of H<sub>2</sub>.

theoretical PDI values were calculated from PP obtained by polymerization in the absence of H<sub>2</sub> and a polymerization time of 120 min in the presence of H<sub>2</sub>. The experimental and theoretical molecular weight distribution curves at polymerization times of 15, 60, 105, and 120 min in the presence of H<sub>2</sub> are shown in Figure 6.

The molecular weight distribution curve was bimodal at short polymerization times in the presence of H<sub>2</sub>. To prolong the polymerization time in the presence of H<sub>2</sub>, the peak in the higher molecular weight region shifted to a lower molecular weight region because of the chain transfer to H<sub>2</sub>. In addition, the bimodal phenomenon was minimized with increasing polymerization time in the presence of H<sub>2</sub>. With regard to short polymerization times (e.g., 15 min) in the presence of H<sub>2</sub>, the experimental curve showed a higher peak in the higher molecular weight region ( $\log M_w \approx 5.7$ ) than the theoretical curve. The reason was that the PP produced did not increase linearly with the polymerization time, and a higher molecular weight PP was obtained at polymerization in the absence of H<sub>2</sub> than in the theoretical one.<sup>10</sup> Thus, the difference between the experimental and theoretical PDI values was higher at shorter polymerization times in the presence of H<sub>2</sub>. However, the errors were diminished for longer polymerization times in the presence of H<sub>2</sub>. Additionally, the theoretical curve shifted to the low-molecular-weight region compared to the experimental one, as shown in Figure 6(d). The reason may have been the decay of the polymerization rate with time: the decay was more serious for longer polymerization times in the presence of H<sub>2</sub>. The decay of the polymerization rate led to an overestimation of the PP fraction obtained in the presence of H<sub>2</sub>. We could change the molecular weight distribution of the obtained PP from 6.6 to 11.6 by changing polymerization time in the presence of H<sub>2</sub>.

## CONCLUSIONS

The catalyst activity decreased with increasing alkyl group size in the cocatalyst, whereas the molecular weight and PDI of PP increased. In addition, the catalyst activity was enhanced by the addition of H<sub>2</sub>. With the introduction of H<sub>2</sub>, the molecular weight and PDI value decreased. The catalyst activity of propylene polymerization increased with increasing polymerization time in the presence of H<sub>2</sub>, whereas the molecular weight decreased. The maximum PDI

of PP was obtained after 60 min of polymerization in the presence of H<sub>2</sub>. In addition, we obtained the bimodal molecular weight distribution curve by changing the polymerization time in the presence of H<sub>2</sub>. We could control the molecular weight and molecular weight distribution of PP by changing the structure of the cocatalyst, H<sub>2</sub> feed, and/or polymerization time in the presence of H<sub>2</sub>.

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