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Control of molecular weight distribution for polypropylene obtained by commercial Ziegler–Natta catalyst: effect of temperature

He-xin Zhang · Young-joo Lee · Joon-ryeo Park · Dong-ho Lee · Keun-Byoung Yoon

Abstract   Polymerization of propylene was carried out by using $MgCl_2$-supported $TiCl_4$ catalyst in conjunction with triethylaluminium (TEA) as cocatalyst. The effect of polymerization temperature on polymerization of propylene was investigated. The catalyst activity was influenced by the polymerization temperature significantly and the maximum activity of the catalyst was obtained at 40 °C. With increasing the polymerization temperature, the molecular weight of polypropylene (PP) drastically decreased, while the polydispersity index (PDI) increased. The effect of the two-stepwise polymerization procedure on the molecular weight and molecular weight distribution of PP was studied and the broad PDI of PP was obtained. It was also found that the PDI of PP could be controlled for propylene polymerization through regulation of polymerization temperature. Among the whole experimental cases, the M_w of PP was controlled from 14.5×10^4 to 75.2×10^4 g/mol and the PDI could be controlled from 4.7 to 10.2.

H. Zhang
Laboratory of Polymer Engineering, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, People's Republic of China

H. Zhang · K.-B. Yoon (✉)
Department of Polymer Science and Engineering, Kyungpook National University,
Daegu 702-701, Korea
e-mail: kbyoon@knu.ac.kr

Y. Lee · J. Park
Catalyst & Process Development Division, R&D Center Samsung Total Petrochemicals Co. Ltd.,
Chungnam 356-874, Korea

D. Lee
Dongyang Mirae University, Seoul 152-714, Korea

Introduction

The world market for polypropylene (PP) was currently over 30×10^6 metric tons/year, and more than 90% world production of PP was produced by Ziegler–Natta catalyst system [1, 2]. Most of the PP produced based on the market needs was manufactured using traditional Ziegler–Natta catalysts which typically comprise $TiCl_4$ supported on $MgCl_2$ through various chemical modifications [1, 2].

In propylene polymerization by $MgCl_2$-supported Ti-based catalysts, hydrogen (H_2) was known to be the most efficient industrial regulator of the molecular weight of the propylene polymerization as chain transfer agent [3]. The use of H_2 as molecular weight regulator was based on the hydrogenolysis of metal to polymer bonds and the rate of chain transfer to H_2 was substantially higher than chain transfer to olefin or alkylaluminium [3, 4].

The properties of PP were influenced by the polymerization condition significantly, such as polymerization time [5], temperature [6], H_2 feed ratio [3, 7], catalyst and cocatalyst concentration or their feed ratio [8]. As reported by Kojoh et al. [9], the catalyst activity and molecular weight decreased with the increasing polymerization temperature, while the molecular weight distribution was broadened for polymerization of propylene under $MgCl_2$-supported $TiCl_4$ catalyst system.

Molecular weight and molecular weight distribution were important factors in determining the physical, mechanical, and rheological properties of polymers [10]. The molecular weight controls the mechanical properties of polymers and molecular weight distribution mainly controls the rheological properties [11]. The molecular weight was controlled by H_2 [7], temperature [6], and polymerization time [5], etc, while the molecular weight distribution was controlled by the methods of physical blending of the polymers with different average molecular weight [12], cascade reactor process [13], and mixing or hybrid of different catalysts [14]. However, the methods of control molecular weight distribution more or less have some defects such as gelation, high cost and complex manipulation, etc [12]. Therefore, it is necessary and interesting to seek a single polymerization system or condition to control the molecular weight and molecular weight distribution of PP.

Therefore, the aim of the present work was to study the effect of polymerization temperature on catalyst activity, isospecificity, molecular weight and molecular weight distribution of PP by using $MgCl_2$-supported Ti-based catalyst system. The two-stepwise polymerization procedure was used to control the molecular weight distribution of PP.

Experimental

Materials

The $MgCl_2$-supported Ti-based catalyst (internal donor: DiBP) and external donor (cyclohexyldimethoxymethylsilane (CHDMMS)) were provided by Samsung Total

Petrochemicals Co., Ltd., Korea. Polymerization grade propylene and triethylaluminium (TEA, 1.0 M solution in *n*-hexane) were provided by Korea Petrochemical Ind. Co., Ltd., Korea. *n*-Hexane was distilled from sodium/benzophenone under nitrogen prior to 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 (TEA) was added to the reactor. After cocatalyst was added, the external donor and catalyst (suspension in *n*-hexane) were injected, respectively, and then the polymerization started with a continuous feed of propylene and H_2 ($V_H:V_P = 0.05$). The pressure was kept constant throughout the polymerization through use of a bubbler and the reaction temperature was controlled by using a water bath. With regards to the two-stepwise polymerization temperature system, the polymerization was started at a lower temperature for 1 h, and then the polymerization temperature was changed to a higher temperature for 1 h polymerization. After a desired time, the polymerization was terminated by adding 10% HCl–methanol solution, and then the mixture was poured into 500 mL of methanol to precipitate the polymer and followed by drying under vacuum at 60 °C to its constant weight. Based on the weight of the obtained polymer, the catalyst activity (kg-polymer/mol-Ti h) was calculated.

Characterization

The polymer product was fractionated by extraction with boiling *n*-heptane for 8 h to determine the isotactic index (I.I.) and the I.I. values reported for each samples were the weight percentage of *n*-heptane insoluble polymer.

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

Calculation of theoretical PDI

Two hypothetical polymers (A and B polymer) with different molecular weights were used to describe the calculation process. The calculation of theoretical PDI was described as following: (1) to unify the total amount of polymer fraction in GPC curves (Fig. 1a, Area$_A$ = Area$_B$); (2) to decide the related amount of A and B fraction to the combined GPC curve, e.g. the yield of A is 2 g and B is 1 g, when the polymerization system is the mixture of A and B at 1:1 feed ratio, the obtained polymer will contain 1 g A polymer and 0.5 g B polymer in theory; (3) to combine the curve of A and B according to the following process:

Fig. 1 The **a** hypothetical GPC curves of A and B polymer and **b** theoretical curve of polymer mixture (A:B = 1:1)
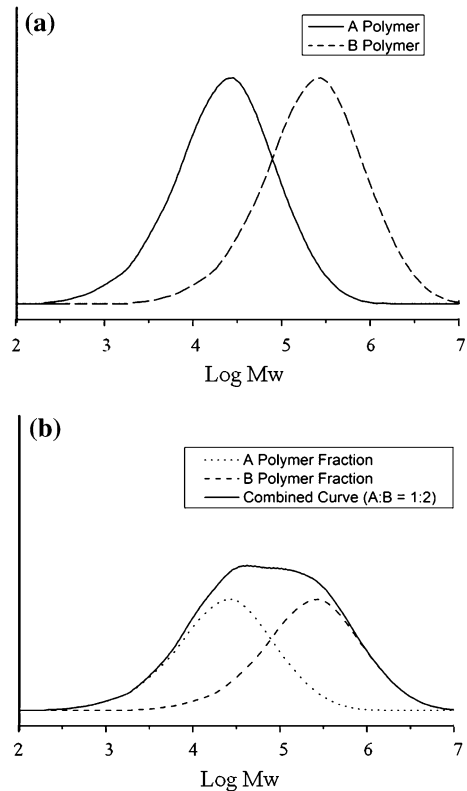
$$y_1 = y_A \times A_A/(A_A + A_B) \tag{1}$$

$$y_2 = y_B \times A_B/(A_A + A_B) \tag{2}$$

$$y_{Combined} = y_1 + y_2 \tag{3}$$

where y_A and y_B are y-axis of GPC curves obtained from A and B polymer (Fig. 1a). A_A and A_B are related amount of A and B polymer in the final polymer. The $y_{Combined}$ is the y-axis of the theoretical GPC curve. The combined GPC curve was shown in Fig. 1b. The theoretical PDI was calculated from the combined GPC curve [15].

Results and discussion

The polymerization of propylene was carried out by using MgCl$_2$-supported TiCl$_4$ catalyst in conjunction with TEA as cocatalyst. The polymerization behavior was examined for various polymerization temperature, 10 °C, 25 °C, 40 °C, 55 °C, and two-stepwise polymerization temperature. H$_2$ was usually used in the industrial polymerization process to regulate the molecular weight of the polymer and external donor was used to improve the isospecificity of obtained PP. Therefore, the polymerization was carried out in the presence of H$_2$ and alkoxysilane compound.

Table 1 Effect of polymerization temperature on propylene polymerization

Polymerization temperature (°C)	Activity (kg-polymer/g-Ti h)	Theoretical activity[a]	I.I. (wt%)	M_w ($\times 10^{-4}$ g/mol)	PDI	Calculated PDI
10	1.5	–	97.6	75.2	4.7	–
25	2.8	–	96.8	44.8	5.1	–
40	3.6	–	97.2	33.3	5.4	–
55	2.7	–	95.9	14.5	5.6	–
10 → 25	2.0	2.2	96.4	57.2	5.7	5.3
10 → 40	2.6	2.6	96.8	49.9	6.6	6.1
10 → 55	2.2	2.1	96.5	44.5	10.2	9.7
25 → 40	3.3	3.2	96.4	41.0	5.8	5.4
25 → 55	3.3	2.8	95.5	37.8	7.6	7.4
40 → 55	3.6	3.2	95.7	31.0	6.2	6.5

Experimental conditions: [catalyst] = 1.2×10^{-4} mol/L, [Al]/[Ti] = 400, [external donor]/[Al] = 0.1, V_H:V_P = 0.05, atmosphere pressure, 2 h

The effect of polymerization temperature on experimental results was given in Table 1.

With regards to the polymerization among the experimental cases, the maximum value of catalyst activity was obtained at 40 °C. The catalyst activity increased with increasing polymerization temperature from 10 °C to 40 °C. However, the catalyst activity slightly decreased at polymerization temperature higher than 40 °C. The decrease of catalyst activity may be ascribed to the low solubility of propylene monomer at higher polymerization temperature [16]. In addition, the theoretical catalyst activity of two-stepwise polymerization system was calculated according to the following equation and the results were summarized in Table 1.

$$\text{Theoretical Activity} = (A1 + A2)/2, \qquad (4)$$

where $A1$ and $A2$ are the activity of first and second step polymerization, respectively. The difference between calculated and experimental results more or less observed. The yield of PP did not increase with increasing polymerization temperature linearly, because the heating time of a desired temperature was different after the first hour polymerization. With regards to the two-stepwise polymerization temperature systems, the catalyst activity was in the range from 2.0 to 3.6 kg-polymer/g-Ti h.

As can be seen from Table 1, the I.I. value of obtained PP roughly decreased with the increase of polymerization temperature. It was well known that the internal donor could be extracted by the alkylaluminium cocatalyst from the solid catalyst during polymerization and the effectiveness of the extraction process increased with increasing polymerization temperature [17–19]. Thus, it was understandable that the I.I. value decreased with the increase of polymerization temperature. The I.I. value of higher than 95 wt% was obtained in the whole range of this study.

Fig. 2 Molecular weight
distribution curves of PP
obtained by polymerization
at different temperature
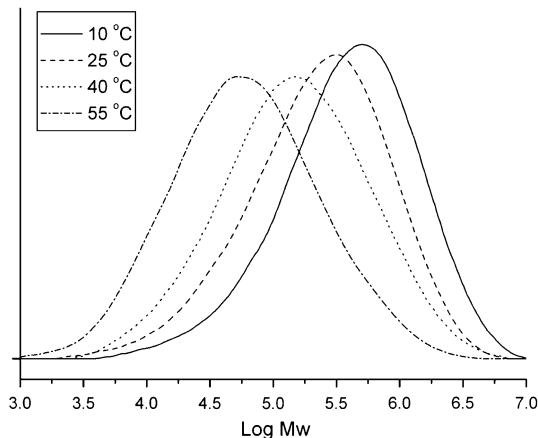
The molecular weight distribution curves of the *n*-heptane insoluble fractions of the samples obtained at different polymerization temperature with MgCl$_2$-supported TiCl$_4$ catalysts were shown in Fig. 2.

The molecular weight of obtained PP decreased with the increase of polymerization temperature, while the PDI value increased slightly. The decreased molecular weight could correspond to the strong chain transfer reaction at higher polymerization temperature [6]. In addition, the decreased molecular weight and increased PDI were reported by Kojoh et al. [9] also. However, the opposite results were observed by Chadwick et al. [20] where the molecular weight increased with the increasing polymerization temperature for propylene polymerization by using MgCl$_2$-supported TiCl$_4$ catalyst (internal donor: DiBP) in presence of external donor. With regards to the one-stepwise polymerization temperature system, the weight-average molecular weight (M_w) of obtained PP was in the range from 14.5×10^4 to 75.2×10^4 g/mol and the PDI value was in the range from 4.7 to 5.6 for one-stepwise polymerization temperature system.

As described before, the PDI slightly increased with the increasing polymerization temperature. In order to produce broad molecular weight distribution of PP, a two-stepwise polymerization temperature was introduced, while the higher molecular weight fraction was obtained at lower polymerization temperature and the lower molecular weight fraction was obtained at higher polymerization temperature. Additionally, with regards to the two-stepwise polymerization temperature systems, the theoretical PDI values were calculated from the combined molecular weight distribution curve of PP obtained by the two different temperatures. The calculation was based on ideal conditions (polymerization yield linear increased with polymerization time and without delay during the temperature change). The ratio of combined molecular weight distribution curve was determined by the ratio of polymer yield of the two different polymerization temperatures respectively. The experimental and theoretical GPC curves were given in Fig. 3.

In the whole range of this study the unimodal molecular weight distribution curves were obtained even at the broad temperature change (10 → 55 °C). Among
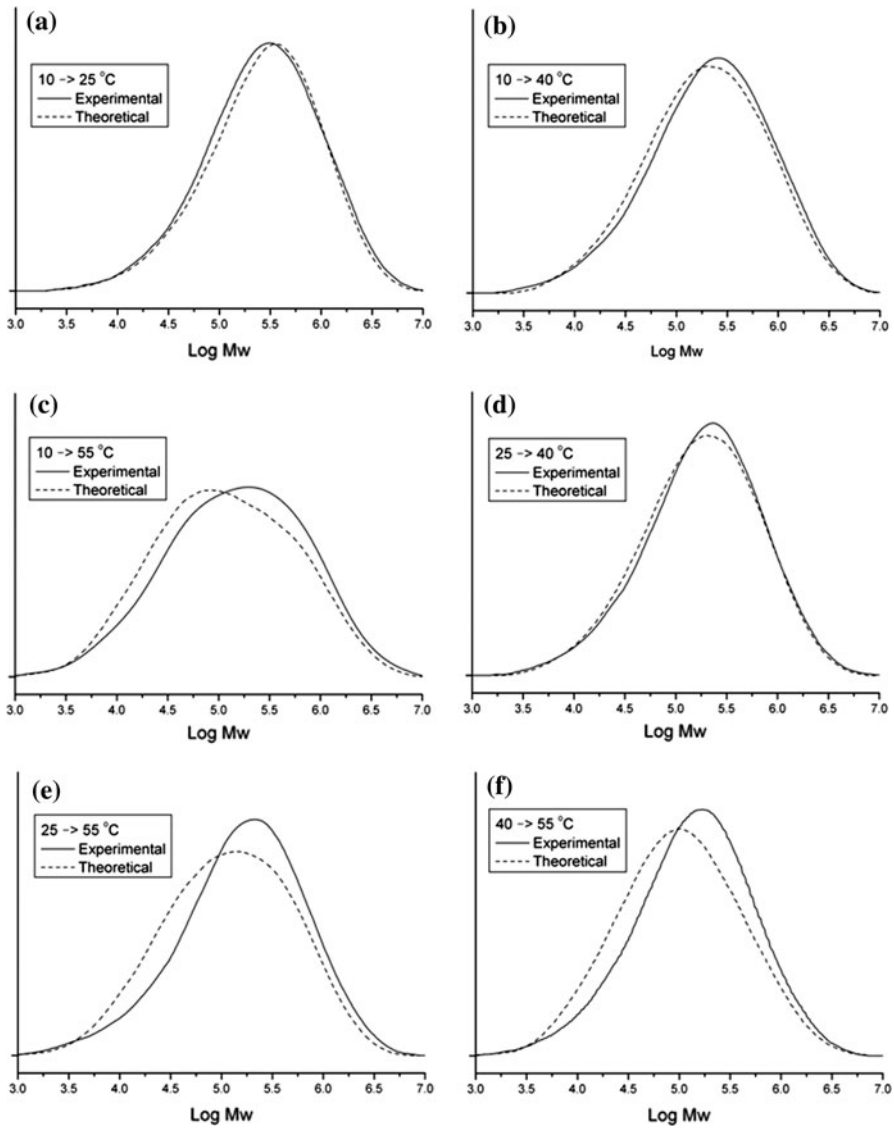
Fig. 3 Experimental and theoretical molecular weight distribution curves of PP obtained by polymerization at two-stepwise polymerization temperature system

the experimental cases, the experimental molecular weight distribution curve slightly shifted to the higher molecular weight part related to the theoretical curve, although the shift was not so clear for the small change in polymerization temperature, e.g. Fig. 3a and d. It was found that the experimental molecular weight was higher than the theoretical one. The reason could correspond to the PP yield not linear increased with increasing polymerization temperature, and more PP product was obtained at lower temperature than the theoretical one [21]. As can be seen in

Table 1, the PDI value of PP obtained by two-stepwise polymerization temperature system was higher than the PP obtained by polymerization at the single polymerization temperature. We suggest that the obtained PP of broad molecular weight distribution including two parts; (1) high molecular weight fraction and (2) low molecular weight fraction. The high molecular weight fraction was obtained at lower polymerization temperature (lower chain transfer reaction), while the strong chain transfer reaction occurred with the increasing polymerization temperature lead to decrease the molecular weight of obtained PP. Thus, the broad molecular weight distribution PP was obtained by a single catalyst and reactor. The highest PDI (PDI = 10.2) of PP was obtained at the broad temperature change (10 → 55 °C). In comparison with traditional physical blending method, the two-stepwise polymerization procedure could save more cost. With regard to Ziegler–Natta and metallocene hybrid catalyst, they suffer from many drawbacks. In particular, alkylaluminium cocatalyst, which is used to activate Zeigler-Natta catalyst, has a serious detrimental effect on metallocene catalysts. In this research, it could be found that the PDI value of obtained PP could be controlled through a single reactor and single catalyst system. Among the two-stepwise polymerization temperature systems, the PDI value was in the range from 5.7 to 10.2 by regulating the polymerization temperature.

Conclusions

The catalyst activity in the propylene polymerization was influenced by the polymerization temperature significantly. The maximum activity of the catalyst was obtained at 40 °C. The catalyst activity increased with increasing polymerization temperature from 10 °C to 40 °C. The polymerization temperature higher than 40 °C resulted in lower catalyst activity. With increasing the polymerization temperature, the molecular weight of PP drastically decreased, while the T_m and X_c, as well as PDI increased. In addition, the PDI of PP could be broadened by introduction of two-stepwise polymerization temperature system. Among the whole experimental cases, the unimodal molecular weight distribution curves were obtained. It showed that the molecular weight and molecular weight distribution of PP could be controlled and predicted by changing the polymerization temperature. By regulating the polymerization temperature, the M_w of PP was in the range from 14.5×10^4 to 75.2×10^4 g/mol and the PDI value was in the range from 4.7 to 10.2.

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