

Effect of Polymerization Time on the Molecular Weight and Molecular Weight Distribution of Polypropylene

S. Abedi,¹ M. Hosseinzadeh,² M. A. Kazemzadeh,¹ M. Daftari-Besheli¹

¹Petrochemical R and T of NPC (Arak Center), P.O. Box 1493, Arak, Iran

²Arak Petrochemical Co., Arak, Iran

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ABSTRACT: The influence of the polymerization time on the molecular weight (M_w , M_n , M_p , and M_z), molecular weight distribution (MWD) and relative MWD of polypropylene (PP) in the propylene polymerization with a $Mg(OEt)_2/DIBP/TiCl_4/PTES/AlEt_3$ catalyst system in the slurry phase has been studied by using gel permeation chromatography (GPC), where $Mg(OEt)_2$, DIBP (diisobutyl phthalate), $TiCl_4$, PTES (phenyl triethoxy silane), and tri-

ethyl aluminum (TEA) are support, internal donor, catalyst, external donor, and cocatalyst, respectively. It has been found that the increase of the polymerization time increases the molecular weight and MWD of PP. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 368–371, 2006

Key words: PP; Ziegler–Natta Polymerization; GPC

INTRODUCTION

Highly active Ziegler–Natta catalysts obtained by combining a component comprising a magnesium compound and a titanium compound with an activating organoaluminum compound were reported and have gained significant industrial importance in the recent years, because the improved activity has eliminated catalyst removal procedures after polymerization.^{1–7}

Propylene polymerization was investigated with the catalytic system $Mg(OEt)_2/DIBP/TiCl_4/PTES/AlEt_3$.^{5–9} These kinds of catalyst systems are used in some industrial process and give high activity and selectivity. The effect of various parameters such as polymerization temperature, monomer pressure, polymerization time and the amount of triethyl aluminum (TEA), hydrogen (as a chain transfer agent), internal and external donors on the catalyst activity, and stereoselectivity was reported in the literature.^{5–11}

Polymer residence time in the polymerization reactors is one of the most important parameters that should be exactly calculated and also controlled in the industrial plants, because it has a noticeable effect on the catalyst activity (it decreases with increase in the polymerization time).^{7–10} Since the molecular weight of polypropylene and its distribution have strong effects on the processability and end-use properties of

the propylene polymers, in this article, we present the effects of the polymerization time on the number-average molecular weight (M_n), weight-average molecular weight (M_w), molecular weight distribution (MWD), and relative MWD (the ratio of two MWDs in the two consecutive period of the polymerization time) in propylene polymerization by using a $Mg(OEt)_2/DIBP/TiCl_4/PTES/AlEt_3$ catalyst system. The other averages defined as M_p and M_z have also been studied in this article.^{12,13}

This investigation has showed that the polymerization residence time has a remarkable effect on the molecular weight and MWD of the produced polymers. Such results can be of interest for polyolefins producers to mind the effects of polymerization residence time on molecular weight and MWD as well as catalyst activity.

EXPERIMENTAL

Materials

Propylene (polymer grade), nitrogen (>99.99%), and *n*-hexane ($H_2O < 2$ ppm) were purchased from Arak Petrochemical Co. (Iran). $TiCl_4$, TEA, PTES, and DIBP were purchased from Fluka Co. (Switzerland). Magnesium ethoxide and toluene (extra pure grade) were purchased from Merck Co. (Germany). *n*-Heptane ($H_2O < 3$ ppm) was prepared from Shazand Refinery Co. (Iran).

Catalyst

Ten grams of $Mg(OEt)_2$ and 20 mL of $TiCl_4$ were added to 80 mL of toluene in a 1.0-L flat-bottom flask,

Correspondence to: S. Abedi (s.abedi@npc-rt.ir).

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TABLE I
Effect of Polymerization Time on Molecular Weight of Polymer

| Polymerization time (h) | M_w | M_n | M_p | M_z | MWD |
|-------------------------|---------|--------|---------|---------|------|
| 1 | 99,960 | 26,930 | 78,742 | 303,539 | 3.71 |
| 2 | 106,827 | 28,425 | 87,025 | 315,759 | 3.76 |
| 3 | 118,126 | 30,390 | 98,559 | 325,413 | 3.89 |
| 4 | 153,661 | 36,492 | 122,677 | 479,469 | 4.21 |

under vigorous stirring with a magnetic stirrer in room temperature. Then, the temperature of the mixture was increased to 115°C in 1 h. Upon reaching 90°C, 2.7 mL of DIBP as the ID was added.

The temperature was maintained at 115°C for 2 h, it was then left to decant and afterwards the hot liquid was siphoned off. The solid product was washed with 100 mL of toluene and then treated with 20 mL of $TiCl_4$ for 2 h. Finally, it was left to settle and the liquid was siphoned off while hot; the residual solid washed 10 times with 100 mL of hot *n*-hexane until no traces of titanium were detected in the washing liquid.^{10,11,14} The washed catalyst was stored in *n*-heptane in a glovebox, under nitrogen atmosphere.

Polymerization

Polymerization was carried out in a 1.6-L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer (mixing speed was around 500 rpm, T form) in the slurry phase.

After running out of all moisture and air by nitrogen, 800 mL of *n*-heptane was added. After 10 min, 20 mL of TEA (2M in heptane), 2.5 mL of PTES (1M in heptane), and 50 mg of catalyst (dispersed in 2 mL of *n*-heptane) were added by using glass syringes, respectively. Before the catalyst addition, TEA and ED were precontacted for 5 min. The reactor was warmed up to 65–70°C and then propylene was supplied continuously at 9 bar for the required time.

After the polymerization, the untreated gases were slowly released and the polymer was then filtered and dried *in vacuo* at 70°C overnight to a constant weight.

Analysis

The amount of titanium and magnesium elements in the prepared catalyst were determined by atomic absorption spectrophotometer (Shimadzu 6800). A precisely weighed quantity of catalyst (about 100–150 mg) was dissolved in 10 mL of 0.1M sulfuric acid solution and diluted to 100 mL with distilled water. The content of chloride was evaluated according to Volhard's method.^{5,15} The catalyst contained 2.51 wt % Ti, 22.03 wt % Mg, and 55.82 wt % Cl.

The molecular weights and MWDs of the produced polymers were measured by gel permeation chromatography (GPC) (Waters hot temperature instrument, model 150-C). The following operating conditions were used—(1) Four columns: μ -Styragel HT 2, 3, 4, and 5 (7.8 mm \times 300 mm); (2) solvent: 1,2,4-trichlorobenzene (TCB), flow rate: 1.0 mL/min; (3) antioxidant: BHT (2,6-di-*tert*-butyl-4-methylphenol) was used as a stabilizer in TCB at a concentration of 1.0 g/L; (4) concentration of samples: 0.1% (w/v). Dissolution of the sample in the stabilized TCB was carried out by heating at 150°C for 24 h, with gentle agitation; (5) injection volume: 200 μ L; and (6) temperature measured (injection): 150°C. Calibration was made on polystyrene standards with narrow and broad distributions, with the use of the universal calibration procedure.^{5,16,17}

RESULTS AND DISCUSSION

The influence of the polymerization time on various parameters of molecular weight has been shown in Table I. According to Table I, M_n , M_w , M_p , M_z and MWD increase with increase in polymerization time.

With regard to the table, M_n , M_w , and MWD increase from 26,930, 99,960, and 3.71 in 1 h of the polymerization to 36,492, 153661, and 4.21 in that of 4 h, respectively.

The increase in MWD shows that the rate of the increase of M_w during a polymerization is slightly more than that of M_n . On the other hand, relative MWD also increases with increase in the polymerization time. According to Table II, when the polymerization time increases from 1 h to 2 h, the increase of the relative MWD is about 1.01, whereas with increase in the polymerization times from 2 h to 3 h and from 3 h to 4 h, the relative MWDs increase to 1.03 and 1.08, respectively. It shows that the increase of the rate growth of M_w slightly increases with increase in the polymerization time.

Also, Table I shows that M_p and M_z rise from 78,742, and 303539 after 1 h of polymerization to 122677 and 479469 after that of 4 h, respectively. Figure 1 shows GPC curves of the produced polymers in the different times.

Figure 2 shows the activity of the catalyst. As the figure shows, the catalyst activity decreases with increase in the polymerization time. This increase causes

TABLE II
Effect of Polymerization Time on Relative MWD

| Time ratio (h) | Relative MWD |
|----------------|--------------|
| 2/1 | 1.01 |
| 3/2 | 1.03 |
| 4/3 | 1.08 |

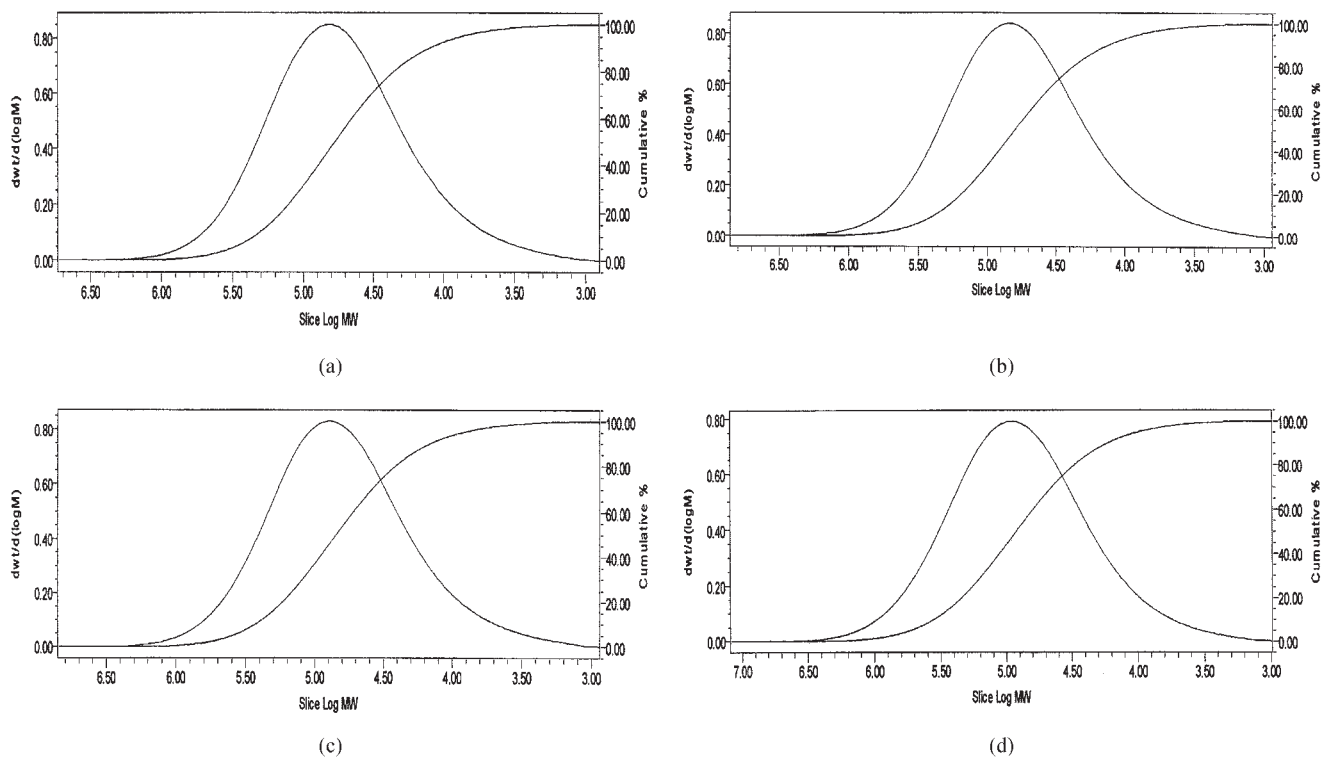


Figure 1 Gel permeation chromatography (GPC) distribution of polypropylene obtained over various times: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h.

the chain transfer to occur late, and consequently, it leads to increase in the molecular weight of the produced polymers.^{7,18–20}

CONCLUSIONS

The increase in the polymerization time causes increase in M_{nr} , M_{w} , M_p , M_z , MWD, and relative MWD.

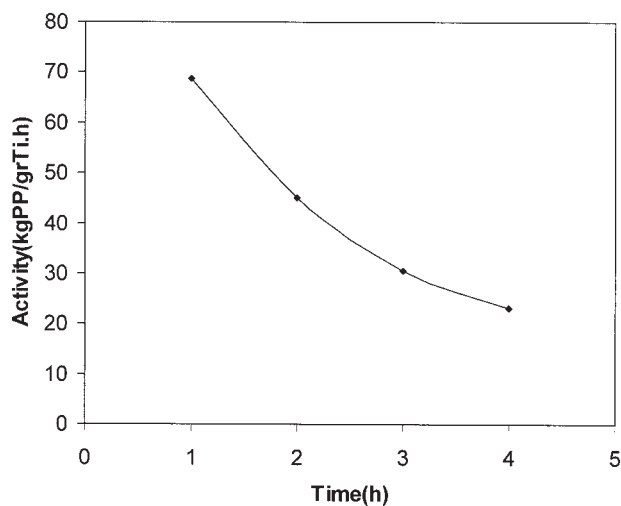


Figure 2 Effect of time on the catalyst activity.

Totally, it has been found that the polymerization time has a remarkable effect on the molecular weight parameters of the produced polymers as well as on the activity of the used catalysts. Therefore, it can have a severe effect on the processibility and properties of the produced polymers. This is why, it is necessary that it should be carefully controlled like the other polymerization factors such as temperature and pressure. Meanwhile, it is possible that the grades of polymers that have slightly broader MWD can be produced with an increase in the polymerization time.

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