

Preparation of Bimodal Polypropylene in Two-Step Polymerization

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ABSTRACT: Polymerization of propylene was carried out by using $\text{MgCl}_2\cdot\text{EtOH}\cdot\text{TiCl}_4\cdot\text{DIBP}\cdot\text{TEA}\cdot\text{cHMDMS}$ catalyst system in *n*-heptane, where MgCl_2 , EtOH, TiCl_4 , DIBP (diisobutyl phthalate), TEA (triethyl aluminum), and cHMDMS (cyclohexyl methyl dimethoxy silane) were support, ethanol for alcoholation, catalyst, external donor, cocatalyst (activator), and internal donor, respectively. The catalyst activity and polymer isotacticity were studied by measuring the produced polymer and its solubility in boiling *n*-heptane, respectively. The molecular weight and molecular weight distribution of the polymers were evaluated by gel permeation chromatography. Hydrogen was used for controlling the molecular weight. For producing the bimodal polypropylene, the polymerization was carried out in two

steps (i.e., in the presence and absence of hydrogen). It was found that the catalyst showed high activity and stereoselectivity, on the other hand, bimodal polymer could simply be produced in two-step polymerization by using $\text{MgCl}_2\cdot\text{EtOH}\cdot\text{TiCl}_4\cdot\text{DIBP}\cdot\text{TEA}\cdot\text{cHMDMS}$ catalyst system. Meanwhile, the effect of the step of the hydrogen adding on propylene polymerization was investigated. It was shown that the addition of hydrogen in the second step was more suitable. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1456–1462, 2006

Key words: Ziegler–Natta polymerization; polypropylene; GPC; molecular weight distribution

INTRODUCTION

The molecular weight distribution (MWD) of the polyolefins is a fundamental property that determines the properties of the polymer and its applications. It is generally recognized that the MWD of a polyolefin resin can principally determine the physical and in particular, mechanical properties of the resin.^{1–7}

For certain applications of the polyolefins, toughness, strength, and environmental stress cracking resistance are important considerations. These properties are enhanced when the polyolefin has high molecular weight. However, as the molecular weight of the polymer increases, the processability of the resin usually decreases. On the other hand, a broadening in the MWD tends to improve the flow of the polymer when it is being processed at the high rates of share. Therefore, by providing a polymer with a broad or bimodal MWD, the properties characteristic of high molecular weight resins are retained and processability, particularly extrudability, is improved.^{1–2,5–9}

The MWD can be completely defined by means of a curve obtained by gel permeation chromatography.

Generally, the MWD is defined by a parameter that is the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n). For most applications, the MWD varies between 5 and 30.⁵

Bimodal MWD of a polyolefin indicates that the polyolefin resin comprises two components of different molecular weight, and implicitly requires a relatively high molecular weight component and low molecular weight component. Totally, the high molecular fraction provides good mechanical properties to the polyolefins and the low molecular weight is required to give good processability to the polyolefins (since the high molecular weight fraction has relatively high viscosity, it can lead to difficulties in processing). In a bimodal polyolefin, the mixture of the high and low melting weight fractions is adjusted as compared to a monomodal distribution so as to increase the proportion of high molecular weight species in the polymer. This improves the polymer properties.^{5–8} A number of approaches have been proposed to produce polyolefin resins with broad or bimodal MWDs.

The first approach is melt blending, in which polyolefins of at least two different molecular weights are blended together before or during processing. These physically produced blends usually contain high gel levels, and consequently, they are not used in the film and other resin applications because of deleterious product appearance due to those gels. In addition, this

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procedure of physically blending resins suffers from the requirement for complete homogenization and attendant high cost. Meanwhile, it is known in the art that it is not possible to prepare polyolefin having a broad MWD and the required properties simply by mixing polyolefins having different molecular weights.^{9–11}

The second one is the use of a mixed hybrid catalyst system in a single reactor. The mostly mixed hybrid catalysts usually contain Ziegler–Natta and metallocene catalyst components. These mixed or hybrid catalyst systems typically comprise a combination of a heterogeneous Ziegler–Natta catalyst and a homogeneous metallocene catalyst. These mixed systems can be used to prepare polyolefins having broad MWD or bimodal polyolefins, and they provide a means to control the MWD and polydispersity of the polyolefin. In spite of the remarkable advantages of the use of supported Ziegler–Natta and metallocene mixed systems for the production of bimodal polyolefins, they suffer from many drawbacks. In particular, triethyl aluminium (TEA), which is used to activate Ziegler–Natta catalyst, has a serious detrimental effect on metallocene catalysts.^{12–17}

The third strategy to making bimodal polymers is the use of multistage polymerization. Such a process relies on two or more polymerization steps or reactor set up, whereby in one polymerization step or reactor, one of the two components of the bimodal blend is produced under a certain set of conditions, and then the second component is produced with a different molecular weight in the second step of the polymerization, under a different set of conditions. These bimodal polyolefins are capable of solving the problems associated with gels and mixed catalysts. In this approach, the high amount of the used hydrogen decreases the catalyst activity. Also, this type of broadening allows the branching to be selectively placed into the high molecular weight portion of the distribution.^{15,17}

The present study reports on $\text{MgCl}_2 \cdot \text{EtOH} \cdot \text{ID} \cdot \text{TiCl}_4$ catalyst system for the production of polypropylene, in particular, such a polypropylene having a bimodal MWD using two-step polymerization approach. The characterization of the resulting products is also reported. In most articles, the GPC curve of bimodal polyolefins shows only a small shoulder and the obtained MWDs are not very broad, whereas it has been shown in this article that the bimodal polymers can be produced by using the high amount of hydrogen, which enjoy a very broad MWD and also their GPC curves show almost very wide peaks. Meanwhile, the effect of the hydrogen injection step has been considered. On the other hand, the effect of hydrogen on the activity and stereoselectivity of the catalyst has also been discussed. Such results can be of interest for

polypropylene commercial producers and researchers in this field.

EXPERIMENTAL

Materials

Propylene (polymer grade), nitrogen (>99.99%), and *n*-hexane ($\text{H}_2\text{O} < 2$ ppm) were purchased from Arak Petrochemical Co. (Iran). TiCl_4 , TEA, and cHMDMS were purchased from Fluka Co. (Switzerland). DIBP, EtOH, Kerosene and toluene (extra pure grade) were purchased from Merck Co. (Germany). Anhydrous Magnesium chloride and *n*-heptane ($\text{H}_2\text{O} < 3$ ppm) were prepared from Toho Titanium Co. (Japan) and Shazand Refinery Co. (Iran), respectively.

Support preparation

At 10°C, 5 g of anhydrous MgCl_2 and 8.2 g of EtOH were added to 250 mL of kerosene in a 1.6-L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer. The mixture was vigorously mixed while the temperature was increased to 120°C and then rotated at 2500 rpm for 10 min and then, the mixture was transferred by a pipe (an inner diameter of 1 mm and a length of 3 m through heaving hot sleeve) to a 2-L flask containing 1000 mL of heptane at –40°C. The precipitate was filtered and then washed three times with 100 mL of anhydrous *n*-hexane.^{18–23} The support was dried and stored under N_2 atmosphere.

Catalyst preparation

The prepared support (10 g) and 50 mL of toluene were added to a 1.0 L special glass reactor having sinter filter in the bottom, equipped with an anchor agitator and previously purged with nitrogen flux. At 10°C, 100 mL of TiCl_4 was added dropwise for 0.5 h under vigorous stirring and then, the temperature of the mixture was increased to 120°C in 1 h. Upon reaching 80°C, 2.4 mL of DIBP were added.

The temperature was maintained at 120°C for 2 h and then, it was hot-filtered. The solid product was treated with 100 mL of TiCl_4 for 2 h. Finally it was filtered while hot; the residual solid was washed five times with 100 mL of hot *n*-hexane until no traces of titanium were detected in the washing liquid.^{18,21–25}

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.

TABLE I
Effect of Hydrogen on the Catalyst Activity and Stereoselectivity

Polymerization no.	Amount of H ₂ (mL)	Activity (kg polypropylene per g catalyst)	I.I. (wt %)
1	0	14.68	96.22
2	1050	15.43	95.61
3	2105	12.24	94.92
4	3131	7.07	94.73
5	4121	4.23	94.36
6	1037	12.19	94.60
7	2112	8.27	94.91
8	3156	5.38	95.31
9	4127	3.31	94.68
10	4057	10.71	94.38

After running out of all moisture and air by nitrogen, 800 mL of *n*-heptane was added. After 10 min, 4 mL of TEA (1M in heptane), 1 mL of cHMDMS (0.18M in heptane), and 10 mg of catalyst (dispersed in 2 mL of *n*-heptane) were added by using dried glass syringes. Before the catalyst addition, TEA and cHMDMS were precontacted for 5 min. The reactor was warmed up to 70°C and then propylene was supplied continuously at 9 bar. In the polymerization in which hydrogen was used, hydrogen was injected at the required amount (Table I) by using a Buchi pressure-flow gas controller before propylene was supplied.

For producing bimodal polypropylene, polymerization was carried out in two steps. At the first step, the required amount of hydrogen was first added and then propylene was supplied. After 1 h of the polymerization, the untreated gases were evacuated. At the second step, the polymerization was continued only in the presence of propylene for 1 h. In the polymerization No. 10, hydrogen was only used in the second step. Meanwhile, the polymerization No. 1 was performed without any hydrogen.

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 amounts 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.^{25–26} The content of chloride was evaluated according to Volhard's method (Table I).²⁵ The catalyst contained 2.1 wt % Ti, 17.43 wt % Mg, and 58.82 wt % Cl.

The molecular weights and MWDs of the produced polymers were measured by GPC (Waters instrument, model 150-C). The following operating conditions

were used: (1) four columns: μ -Styragel HT 2, 3, 4, and 5 (7.8 × 300 mm²); particle size: 10 μ m; (2) solvent: 1,2,4-trichlorobenzene (TCB), flow rate: 1.0 mL/min; (3) antioxidant: BHT (2,6-di-*tert*-butyl-4-methylphenol) at a concentration of 1.0 g/L as a stabilizer in TCB; (4) concentration of samples: 0.1% (w/v) (dissolution of the sample in stabilized TCB was carried out by heating at 150°C for 24 h with gentle agitation); (5) injection volume: 200 μ L; (6) temperature measured (injection): 150°C. Calibration was made with a board MWD standard method on polystyrene standards with narrow and broad distributions, with the use of the universal calibration procedure.^{27–28}

Polymer fractionation

The atactic fraction of polymers was measured by extracting the polymers for 6 h with boiling *n*-heptane in a Soxhlet-type apparatus. The boiling-insoluble fraction is isotactic polypropylene, and the boiling-soluble fraction is atactic. The recovered fractions were dried at 70°C to constant weight. The weight percent of *n*-heptane-insoluble polymer in a whole sample is referred to as the isotactic index (I.I.).^{29–30}

Characterization

The surface area and pore radius of the catalyst were measured by using BET method (NOVA2000 Quantachrome apparatus).³¹ The surface area and average pore radius of the catalyst were 199.89 m²/g and 22.90 Å, respectively.

Catalyst activity was determined in terms of the produced polypropylene (kg) per the used catalyst (g) in the polymerization. MFI of polymers was evaluated by using a Zwick 4100 (ASTM D 1238).³²

RESULTS AND DISCUSSION

Catalyst behavior

A TiCl₄ catalyst supported on MgCl₂ is the representative Ziegler–Natta catalyst used in many processes to produce a high isotactic polypropylene. The MgCl₂.EtOH.TiCl₄.DIBP.TEA.cHMDMS catalyst system usually not only shows high activity and stereoselectivity but also enjoys a good morphology.^{5–6,33–34}

Hydrogen is usually used for controlling the molecular weight of polypropylene in the coordination polymerization as a chain transfer agent.^{35–38}

The effect of hydrogen on propylene polymerization by using the above catalyst system was shown in Table I. As the table shows, the activity of the catalyst slightly increased by increasing in the amount of the added hydrogen and then noticeably decreased. For example, the catalyst activity was 14.68 kg PP/g cat in the absence of hydrogen, whereas it increased to 15.43 kg PP/g cat in the presence of about 1 L of hydrogen

TABLE II
Effect of Hydrogen on the Molecular Weight and Molecular Weight Distribution of the Produced Polypropylenes

Polymerization no.	Amount of H ₂ (mL)	M _w (10 ⁻⁵)	M _n (10 ⁻⁵)	MWD	Shape of MWD	MFI (g/10 min)
1	0	11.67	1.59	7.32	Unimodal	0.3
2	1,050	1.57	0.32	4.86	Unimodal	135
3	2,105	1.15	0.25	4.67	Unimodal	240
4	3,131	0.82	0.19	4.33	Unimodal	590
5	4,121	0.55	0.13	4.21	Unimodal	650
6	1,037	3.95	0.33	12.08	Bimodal	61
7	2,112	3.36	0.26	12.83	Bimodal	120
8	3,156	3.49	0.28	12.29	Bimodal	72
9	4,127	6.27	0.24	26.57	Bimodal	38
10	4,057	7.24	0.28	25.94	Bimodal	12

and then more addition of hydrogen caused a decrease in the catalyst activity, so it decreased to about 12, 7, and 4 kg PP/g cat in the presence of about 2, 3, and 4 L of hydrogen, respectively. These effects on the polymerization related to bimodal were also observed. Unlike the unimodal polymerization, the primary increase in the catalyst activity in the presence of about 1 L of hydrogen didn't occur. Meanwhile, the decrease in the catalyst activity was slightly more than that of the related unimodal polymerization.

The catalyst activity in the polymerization No. 10, in which the second step of the polymerization was car-

ried out only in the presence of hydrogen (about 4 L), was 10.71 kg PP/g cat. The comparison of the polymerization No. 9 and 10 showed that the step of hydrogen injection had a deep effect on the catalyst activity, so the catalyst activity in the polymerization No. 10 was about three times more than that of the polymerization No. 9, whereas the amount of the used hydrogen was almost the same.

Unlike the remarkable effect of hydrogen on the catalyst activity, its effect on the stereoselectivity of the catalyst was insignificant. On the whole, the catalyst stereoselectivity was very high.

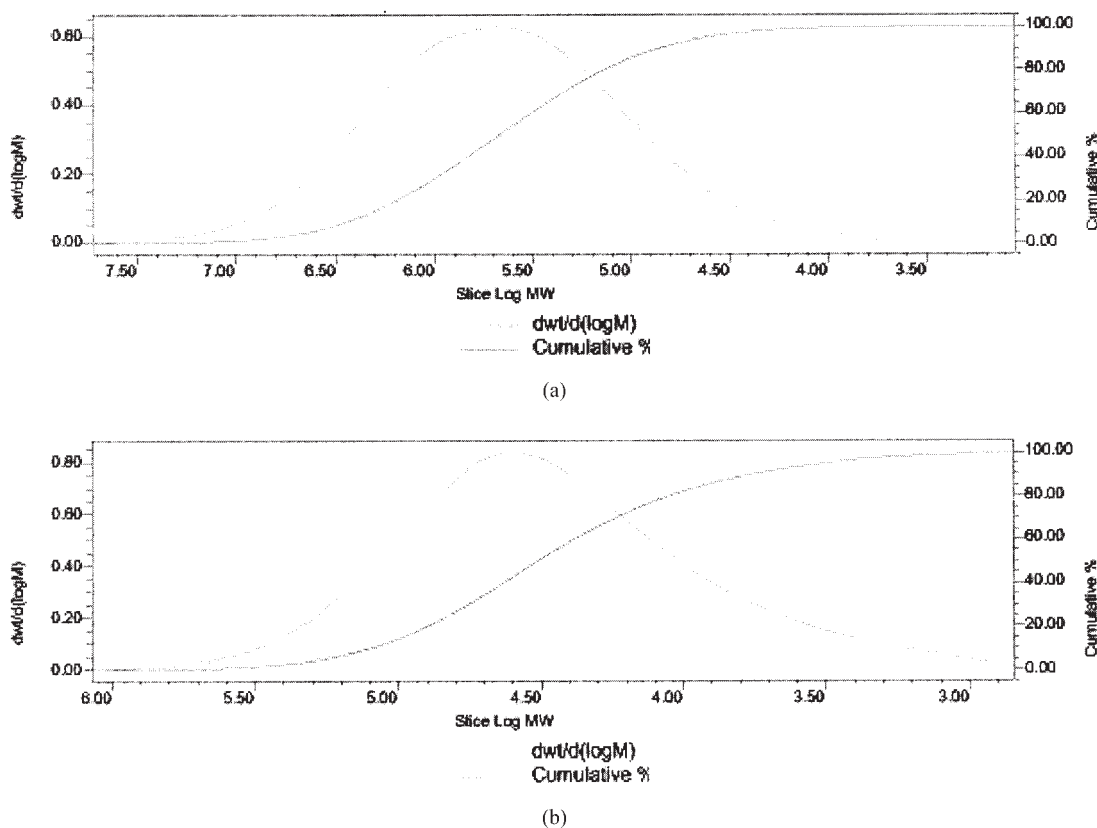


Figure 1 The GPC curves of the unimodal polypropylenes: (a) polymerization no. 1 and (b) polymerization no. 5.

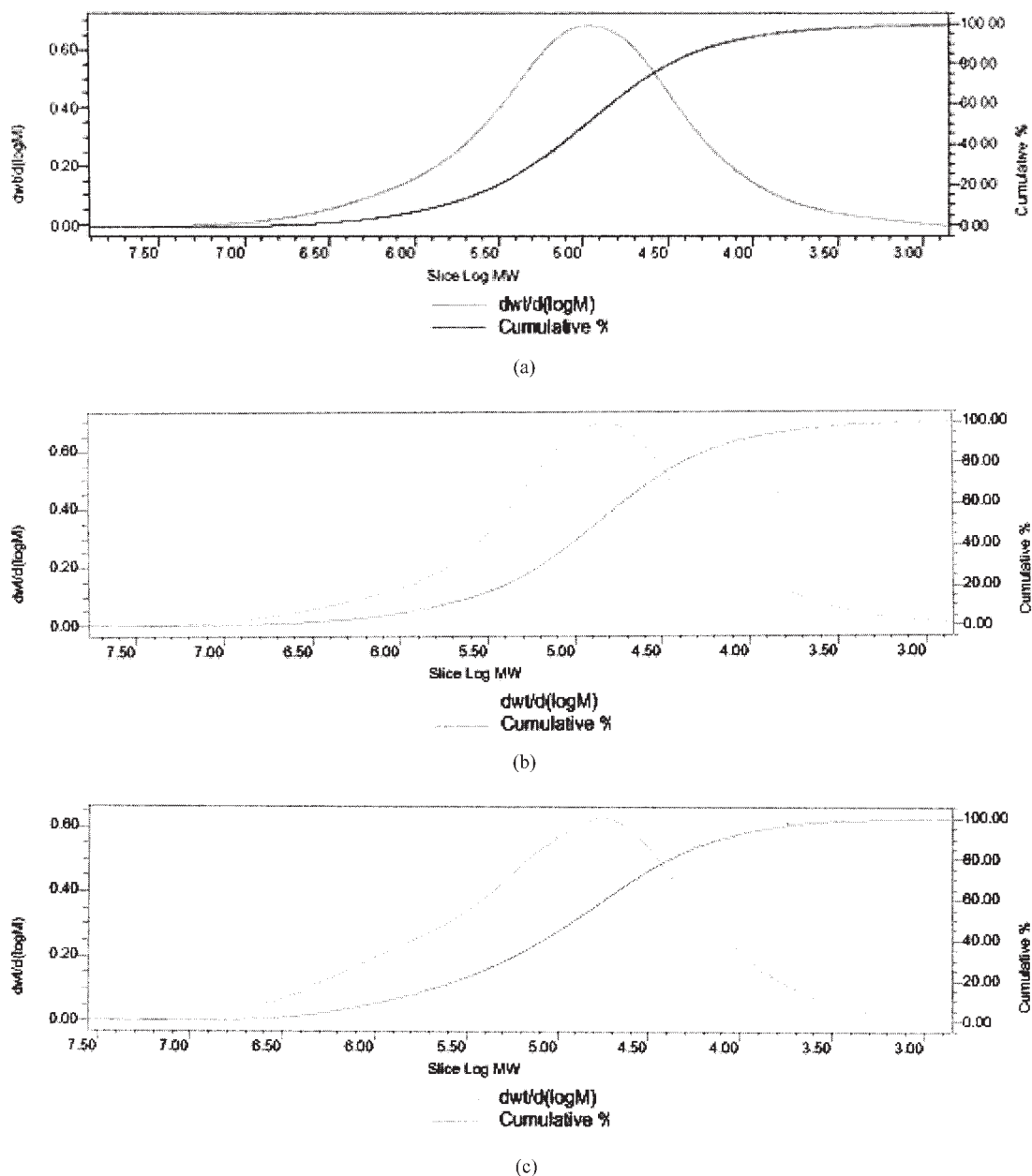


Figure 2 The GPC curves of the bimodal polypropylenes: (a) polymerization no. 6, (b) polymerization no. 7, (c) polymerization no. 8, (d) polymerization no. 9, and (e) polymerization no. 10.

Polymer characterization

Isotacticity

Totally, the produced polymers enjoyed high isotacticity (more than 93%). This tacticity was comparable with most commercial products.

Molecular weight

As mentioned, hydrogen was used for controlling the molecular weight of polyolefins in the coordination polymerization with decrease in the molecular weight.^{5,35–38}

With regard to Table II, the used catalyst was able to produce high molecular weight polypropylene in the absence of hydrogen ($M_w = 11.67 \times 10^5$). The addition of hydrogen to the polymerization system caused a sharp decrease in the molecular weight, which was about 0.55×10^5 in the presence of about 4 L of hydrogen (the polymerization No. 5).

According to the polymerization No. 6–10, the molecular weight of the produced polymers first decreased and then increased with increase in the amount of hydrogen. The reason for increasing was that the produced polymer with high M_w (in the absence of hydrogen) could outshine the produced poly-

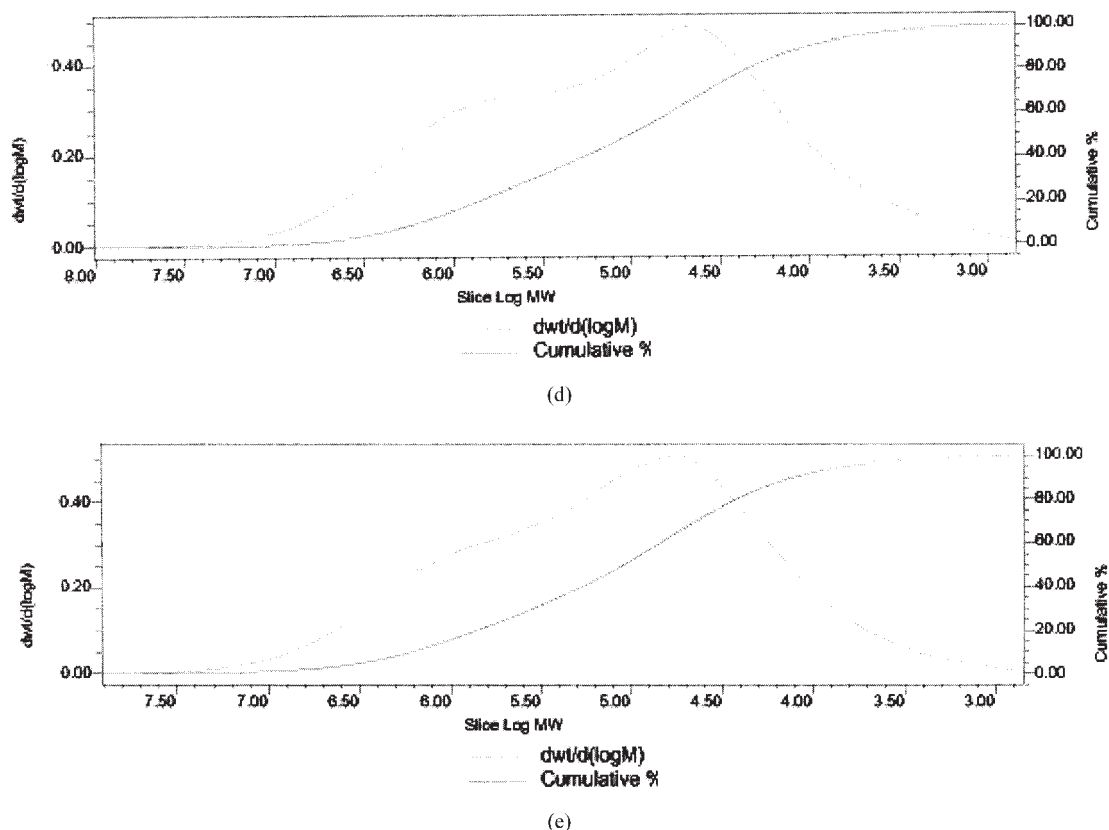


Figure 2 (Continued)

mer with low M_w (in the presence of the high amounts of hydrogen) because the amount of the produced polymer having low M_w was low (because of the drop decrease in the catalyst activity).

Like the M_w , M_n also decreased by the addition of hydrogen; whereas there was no remarkable changes in the M_n of the related bimodal polymerization. Meanwhile, the comparison of the polymerization No. 9 and 10 showed that the step hydrogen injection didn't cause any noticeable difference in the molecular weight of the prepared polymers.

MWD

According to Table II, the MWDs of the unimodal polypropylenes were about 4.21–7.3 (they weren't very broad). On the other hand, it was clear that hydrogen steadily reduced the broadness of MWD; so it decreased from 7.3 to 4.21 in the presence of 0–4 L of hydrogen, respectively.

On the contrary to the unimodal polymers, the MWDs of the bimodal polypropylenes were very broad. Totally, the MWDs of the bimodal PPs were three to seven times wider than that of the unimodal ones.

The comparison of the MWDs obtained from the polymerization No. 9 and 10 showed that the step of the addition of hydrogen didn't have a determining

role in MWD broadening; although the polymerization No. 9 showed slightly a broader MWD.

Shape of MWD

Based on the polymerization procedure, two shapes of MWD were expected.⁶ In the polymerization that was carried out only in one step, the shape of MWD was unimodal (polymerization No. 1–5 in Table II). The GPC curves of the produced unimodal polypropylenes are showed in Figure 1. Whereas in the polymerization that was carried out in two different steps, the broad and bimodal shapes of MWD were expected (polymerization No. 6–10 in Table II). According to Table II, since the bimodal contained a composite of two types of the molecular weight, they had a broad MWD compared with that of unimodal polypropylenes. On the other hand, the GPC curves of the bimodal polypropylenes were different from those of the unimodal ones. In fact, while the curves of the unimodal polypropylenes showed a uniform curve, those of the bimodal ones showed a small shoulder. In particular, polymerization No. 9 and also polymerization No. 10 showed the curves having almost two peaks (Fig. 2).

MFI

As Table II shows, MFI increased with increase in the amount of hydrogen because of the molecular weight decrease in the related unimodal polymerizations.

In the related bimodal polymerization, MFI first decreased and then increased due to the first decrease and then increase of the molecular weight in the produced bimodal polymers.

CONCLUSIONS

The $\text{MgCl}_2 \cdot \text{EtOH} \cdot \text{TiCl}_4 \cdot \text{DIBP} / \text{TEA} \cdot \text{CHMDMS}$ catalyst system showed high activity and stereoselectivity. Hydrogen caused a decrease in the efficiency of the catalyst and its deepest effect was on the catalyst activity. On the whole, the catalyst efficiency was acceptable.

Hydrogen also had a remarkable effect on the molecular weight and MWD of the produced polypropylene; so they decreased with increase in the amount of hydrogen. But, in the polymerization related to bimodal polypropylenes, the molecular weight first decreased and then increased with increase in the amount of the used hydrogen.

It was shown that using two step polymerization, in the absence and presence of hydrogen, the broad or bimodal polypropylene can be produced. Meanwhile, the broadness depends on the amount of the added hydrogen. On the other hand, while the step of the hydrogen addition didn't have a remarkable effect on the MWD, its effect on the catalyst activity was very high; In fact, the MWD of the produced polypropylene from the polymerization in which hydrogen was supplied in the first step was almost the same as MWD of the produced polypropylene from the polymerization in which hydrogen was supplied in the second step, but the obtained catalyst activity in the second case was remarkable more than that of the first one; purposely, hydrogen is used in the second step for producing bimodal polypropylene in two-step polymerization approach.

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