Effect of Polymerization Time and Pressure on the Molecular Weight and Molecular Weight Distribution of Polyethylene

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Abstract: Molecular weight and molecular weight distribution (MWD) of polyethylenes (PE) are important in determining their physical, mechanical, and rheological properties of end-products. In principle, molecular weight controls the mechanical properties of polymers, while MWD mainly affects the rheological properties. Therefore, it is necessary to control molecular weight and MWD to optimize the property and processibility of PE. The conventional Ziegler-Natta catalyst is still the main industrial catalyst for the production of PE. Hence, the control of MWD of PE produced using Ziegler-Natta catalyst has always been one of the most worthy research targets for industry and academy. The influence of the polymerization time and pressure on the molecular weight, MWD and relative MWD of PE in the ethylene polymerization with a $MgCl_2/SiO_2/TiCl_4/AlEt_3$ catalyst system in the slurry phase was studied by using gel permeation chromatography (GPC). It has been found that with the lapse of time increases the molecular weight and MWD of PE. However, the increase of the polymerization pressure increases the molecular weight and decreases the MWD of PE.

Keywords: $MgCl_2/SiO_2$ Bi-support; Ziegler-Natta Catalyst; Polymerization; PE; GPC

1. Introduction

Anhydrous $MgCl_2$ has been known as a preferred support for highly efficient Ziegler-Natta olefins polymerization catalysts, because it can stabilize the active centers and increase the activity of the catalysts[1-4]. The most important step is the preparation of spherical $MgCl_2$. But this process is rather complicated and not easy to control, and the catalyst is apt to break up and produces fine powder during polymerization[5,6]. SiO_2 has also been used as catalysts supports due to its high specific surface areas and good morphology. However, SiO_2 supported titanium catalysts show low activity. While $MgCl_2/SiO_2$ supported $TiCl_4$ catalysts have been widely used for the polymerization/ copolymerization of ethylene and propylene. The improved activity has eliminated catalyst removal procedures after polymerization and the bisupported catalysts are very suitable for controlling the particle sizes of polymers[7-9].

Many $MgCl_2/SiO_2$ bisupported Ti catalysts have been reported for ethylene polymerization. These high activity catalysts systems have gained significant industrial importance in the recent years. The effect of various parameters such as polymerization temperature, monomer pressure, polymerization time and the amount of triethyl aluminum, hydrogen, internal donors on the catalyst activity, and copolymerizability was reported in the literature[10-13].

Polymer residence time and polymerization pressure in the polymerization reactors are two of the most important parameters that should be exactly calculated and also precisely controlled in the industrial plants, because they have a noticeable effect on the catalyst activity (it decreases with increase in the polymerization time, and improves with increase in the polymerization pressure)[5,7,14]. Since the molecular weight of polyethylene and its distribution have strong effects on the processability and end-use properties of the ethylene polymers[10,12], in this article, we present the effects of the polymerization time and the polymerization pressure on the number-average molecular weight (M_n), weight-average molecular weight (M_w), MWD and relative

MWD (the ratio of two MWDs in the two consecutive period of the polymerization time and the polymerization pressure) in ethylene polymerization by using a $MgCl_2/SiO_2/TiCl_4/AlEt_3$ catalyst system.

This investigation has showed that the polymerization residence time and the polymerization pressure have a remarkable effect on the molecular weight and MWD of the produced polymers. Such results are interesting for polyolefins producers who mind the effects of polymerization residence time and polymerization pressure on molecular weight and MWD as well as catalyst activity.

2. Materials and methods

2.1 Materials

All manipulations of the air and moisture sensitive materials were carried out under a dry argon atmosphere with standard Schlenk techniques. $AlEt_3$, $MgCl_2$, and $TiCl_4$ all purchased from Aldrich were used without further purification. Silica 955 from Daqing Petrochemical Company was calcinated at 600 ^{o}C for 4 h under N_2 flow. The solvents were dried according to general procedures before use. Ethylene was purified by passing through oxygen scavenging column and 4 Å/13X molecular sieves.

2.2 Preparation of catalyst

The catalyst was prepared via three steps, including (i) calcination of silica at 600^{o}C (ii) preparation of $SiO_2/MgCl_2 \cdot n$BuOH bi-support, (iii) impregnation of $TiCl_4$ compound on bi-support. These procedures are described in more detail as follows.

(i) Calcination of silica: First, 10 g silica was weighed and put in a quartz bowl, which was then laid into a tube furnace. Under a dry N_2 flow the tube was heated to 600^{o}C within 3 h and was maintained at this temperature for 4 h. Finally the tube was cooled to room temperature, and silica was removed and preserved under N_2 for further use.

(ii) Preparation of $SiO_2/MgCl_2$•nBuOH bi-support: $MgCl_2$ and *n*-butanol (*n*BuOH) in a molar ratio (*n*$MgCl_2$: *n*BuOH) of 1:4 were added into the reactor and an equal volume of *n*-heptane was added. The mixture was heated to 95 ^{o}C and stirred until the $MgCl_2$ was completely dissolved. A prescribed amount of pretreated SiO_2 was introduced into the resulting solution, the mass ratio of SiO_2 and $MgCl_2$ was 5, stirred at 95 ^{o}C for 5 h, then filtered off, washed with *n*-heptane, and finally dried under vacuum to give $SiO_2/MgCl_2 \cdot n$BuOH solid.

(iii) impregnation of $TiCl_4$ compound on bi-support: 50 mL of *n*-heptane and 5 g of bi-support were introduced in 300 mL flask equipped with a magnetic stirrer, and then added 2 mL of $TiCl_4$ dropwise before heating the mixture slowly to 90 ^{o}C. After stirring the mixture for 2 h at 90 ^{o}C, the resulting solid was filtered and washed with *n*-hexane five times at 60 ^{o}C and two times at room temperature. The final catalyst was dried under vacuum.

2.3 Polymerization

Polymerization was carried out in a 2-L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer (mixing speed was around 450 rpm, T form) in the slurry phase. After running out of all moisture and air by nitrogen, 1000 mL of *n*-heptane was added. After 10 min, 1 mL of TEA (1*M* in *n*-heptane), and 10 mg of catalyst (dispersed in 2 mL of *n*-heptane) were added by using glass syringes, respectively. Before the catalyst addition, TEA was precontacted for 5 min. The reactor was warmed up to 60°C and then ethylene was supplied continuously at the required time and pressure. 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.

2.4 Analysis

The amounts of Mg and Cl were measured by titration methods and the amount of Ti was determined by spectrophotometer at 420 nm. The surface area, pore volume, and pore size of support and catalyst were measured by using a standard BET method. The catalyst contained 3.30 wt% Ti, 2.14wt % Mg, and 21.67 wt % Cl with its surface area of 227 m^2/g, pore volume of 0.94 cm^3/g and pore size of 13.6 nm. The molecular weight and MWD of the polymer were determined by a PL-GPC220 gel permeation chromatograph (GPC) equipped with a refractive index detector, viscosimetric detector and a set of Styragel columns (HT6, HT5, and HT3) by using 1,2,4-trichlorobenzene as a solvent at 150 ^{o}C and 1.0 $mL \cdot min^{-1}$.

3. Results and discussion

As summarized in Table 1, the polymerization time leads to a significant change of molecular weight and MWD of polyethylene. M_n, M_w and MWD increase with increase in polymerization time. With regard to the table, M_n, M_w, and MWD increase from 114,014, 849,286, and 7.45 in 0.5 h to 262,405, 2,708,177, and 10.32 in that of 3 h, respectively. The increase in MWD shows that the growth rate M_w during polymerization is slightly faster than that of M_n. On the other hand, relative MWD decreases with increase of polymerization time. According to Table 2, when the polymerization time increases from 0.5 h to 1 h, the decrease of the relative MWD is about 1.103, whereas with increase in the polymerization times from 1.5 h to 2 h and from 2 h to 3 h, the relative MWDs decrease to 1.093 and 1.058, respectively. It shows that the increase of the growth rate of M_w slightly decreases with increase of polymerization time. Figure 1 shows GPC curves of the produced polymers in different times. This increase causes the chain transfer to occur late, and consequently, it leads to increase in the molecular weight of the produced polymers. The catalytic activity is shown in Figure 2. The polymerization conditions of Figure 2 are *n*-heptane 1000mL, [Al]/[Ti]=235, P_E=1 atm, T=60 °C , t=2h. As we can see from the figure 1, the activity of the catalyst decreases with the increase of the polymerization time. The behavior was the same as for $MgCl_2$-supported catalyst for homopolymerization. Because of slurry polymerization and the extension of polymerization time, there are two possibilities for the unexpected behavior: encapsulation of active centers of the catalyst in slurry polymer and the decay of some active centers due to increase of reaction time[15].

Table 1 Effect of polymerization time on molecular weight of polymer

Run	Polymerization Time (h)	M_n (g/mol)	M_w (g/mol)	MWD
1	0.5	114014	849286	7.45
2	1.0	160288	1317702	8.22
3	1.5	216092	1928516	8.92
4	2.0	245054	2390291	9.75
5	3.0	262405	2708177	10.32

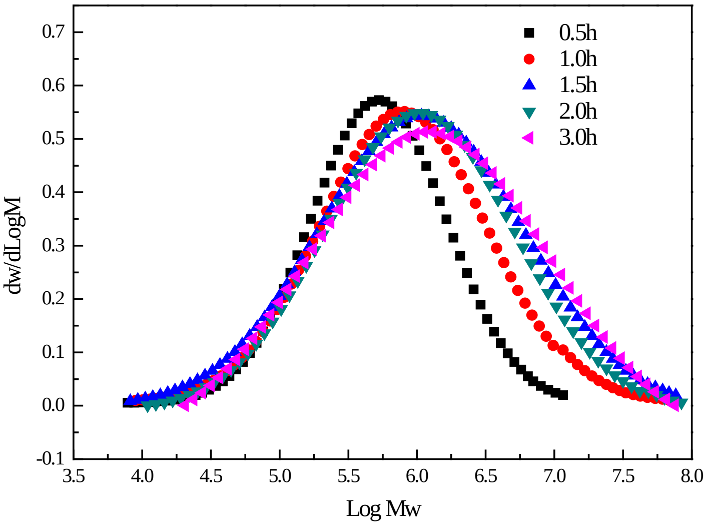

Figure 1 Gel permeation chromatography (GPC) distribution of polyethylene obtained over various times

Table 2 Effect of polymerization time on relative MWD

Time Ratio	Relative MWD
1.0/0.5	1.103
1.5/1.0	1.085
2.0/1.5	1.093
3.0/2.0	1.058

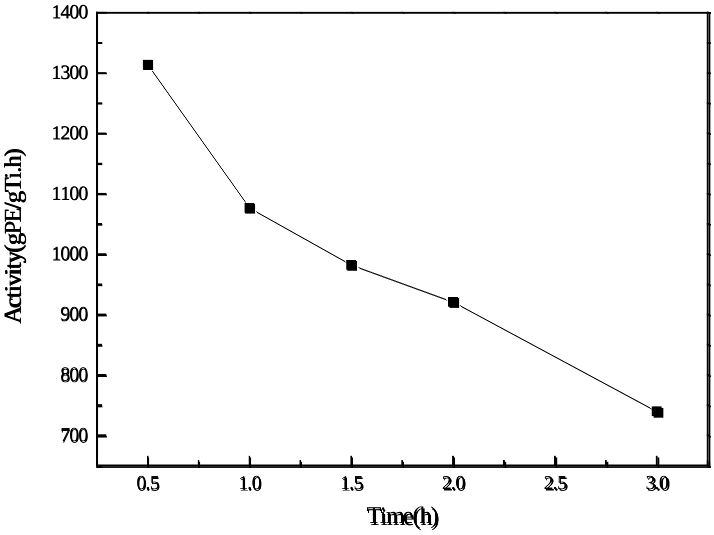

Figure 2 Effect of time on the catalyst activity

The effect of polymerization pressure varied from 0.1 to 1.0MPa on molecular weight and molecular weight distribution has been shown in Table 3. As it can be seen, increasing polymerization pressure sharply increases M_n of the resulting polyethylene. M_n, M_w, and MWD increase from 245,054, 2,390,291, and 9.75 in 1atm of the polymerization to 553,569, 2,731,846, and 4.93 in that of 10 atm, respectively. This phenomenon can be attributed to higher concentration of monomer. The first-order rate of polymerization with the ethylene concentration has been reported for Ziegler–Natta catalysts[15]. M_w of the polymer was increased with the monomer pressure increasing from 0.1 to 0.4 MPa, a further increase of the pressure to 1.0 MPa did have not much effect on the M_w value. An obvious decrease of MWD is observed with increasing the polymerization pressure. The decrease of MWD also shows that the growth rate of M_w during polymerization is slightly less than that of M_n. In contrast, relative MWD increases with increase of polymerization pressure. According to Table 4, when the polymerization pressure increases from 1 atm to 4 atm, the decrease of the relative MWD is about 0.7703. With the polymerization pressure increasing from 4 atm to 7 atm and from 7 atm to 10 atm, the relative MWDs increase to 0.6778 and 0.9686, respectively. This behavior could be explained to a higher concentration of the monomer at active sites, which could, in effect, reduce the role of the chain-transfer reaction to the monomer and TEA. Figure 3 shows GPC curves of the produced polymers in the different pressures.

Figure 4 shows the activity of the catalyst against the monomer pressure. The polymerization conditions are same as Figure 2. As is shown, increasing the monomer pressure sharply increased the catalyst productivity because of the higher concentration of the monomer. This increase causes the chain transfer to occur late, and consequently, it leads to increase in the molecular weight of the produced polymers.

Table 3 Effect of polymerization pressure on molecular weight of polymer

Run	Polymerization Pressure (MPa)	Polymerization Time (h)	M_n (g/mol)	M_w (g/mol)	MWD
6	0.1	2.0	245054	2390291	9.75
7	0.4	2.0	372374	2795891	7.51
8	0.7	2.0	535565	2725767	5.09
9	1.0	2.0	553569	2731846	4.93

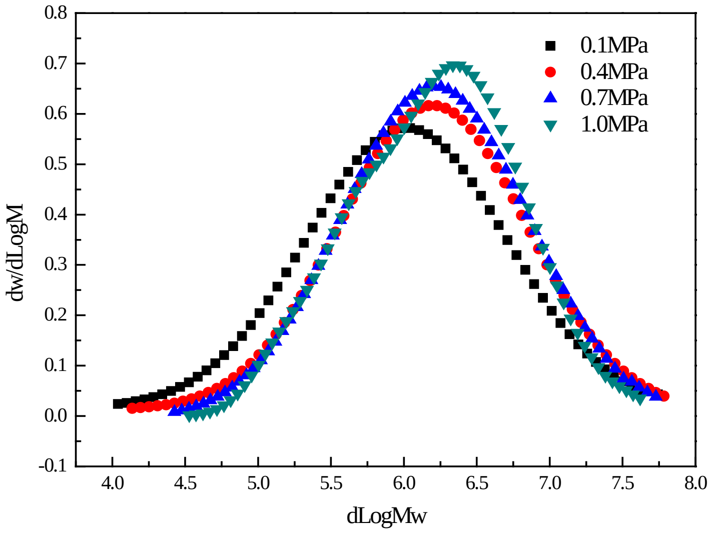

Figure 3 Gel permeation chromatography (GPC) distribution of polyethylene obtained over various pressures

Table 4 Effect of polymerization pressure on relative MWD

Pressure Ratio	Relative MWD
0.4/0.1	0.7703
0.7/0.4	0.6778
1.0/0.7	0.9686

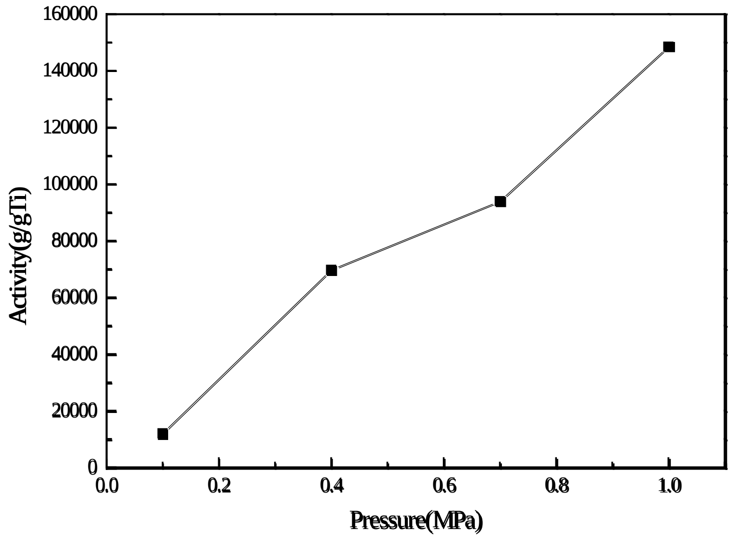

Figure 4 Effect of pressure on the catalyst activity

4. Conclusions

Totally, it has been found that the polymerization time and the polymerization pressure have a remarkable effect on molecular weight of the produced polymers as well as on the activity of the used catalysts. The molecular weight and MWD of polyethylene are important factors in determining the physical, mechanical, and rheological properties of polymers. Therefore, it is necessary to control molecular weight and MWD to optimize the property and processibility of PE. Meanwhile, it is possible that the grades of polymers that have slightly broader MWD can be produced with an increase in the polymerization time or a decrease in the polymerization pressure.

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