

Control of Molecular Weight Distribution (MWD) for Polyethylene Catalyzed over Ziegler-Natta/Metallocene Hybrid Catalysts

Han Seock Cho, Kee Ho Choi, Dae Jung Choi and Wha Young Lee^{*}

Division of Chemical Engineering, College of Engineering, Seoul National University,
Shinlim-Dong, Kwanak-Ku, Seoul 151-742, Korea

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Abstract—Two types of inorganic supports, MgCl_2 and SiO_2 , for the impregnation of catalysts were prepared by the recrystallization and sol-gel methods, respectively. The Ziegler-Natta/Metallocene hybrid catalysts were prepared in order to control the molecular weight (Mw) and the molecular weight distribution (MWD) during ethylene polymerization. The polyethylene produced by the hybrid catalysts can control the Mw and the MWD of polymer, showing two melting temperatures and a bimodal MWD, corresponding to products arising from each of the individual catalysts. This suggests that these hybrid catalysts acted as individual active species and produced a blend of polymers.

Key words: Metallocene Catalyst, Ziegler-Natta Catalyst, Ziegler-Natta/Metallocene Hybrid Catalysts, Ethylene Polymerization, Support

INTRODUCTION

Metallocene catalyst systems, discovered by Kaminsky and Sinn in early 1980, have been focused upon as the next generation of catalysts for olefin polymerization. Such systems show a high activity and are capable of producing polymers with special properties which are unattainable via Ziegler-Natta catalyst systems [Kaminsky et al., 1992; Kaminsky and Renner, 1993]. Although metallocenes have several advantages, the polymers via these catalysts have a narrow molecular weight distribution (MWD). In polymer processing, the molecular weight (Mw) and the MWD are important factors because they determine both the mechanical and the rheological properties, respectively [Kaminsky and Ahlers., 1988]. On the one hand, polyethylenes with narrow MWD lead to products with higher impact resistance and also give a resistance to stress-cracking. On the other hand, polyethylenes with a broad MWD show greater flowability in the molten state at high shear rate, which is important for blowing and extrusion techniques.

Several methods for controlling the Mw and the MWD of polymers are available. The first method is to use a series of reactors, involving different polymerization conditions such as temperature, pressure, and hydrogen partial pressure. However, this method is not acceptable because it involves additional processes and increases capital cost. The second method is to blend the polymers produced by individual catalysts. Although blends can control the Mw and the MWD of polymers, the blends contain high gel level, and, as a result, miscibility problems can occur. And

the third method is to combine two or more transition metal catalysts in a single reactor, thus giving polymers with different Mw ranges. In this case, a highly advanced catalyst technology is needed.

Studies in this area to date have dealt with the use of catalyst mixtures which are homogeneous [Luigi et al., 1998]. However, a limited number of reports have been published which deal with MWD in heterogeneous types [Cho et al., 1998, 1999]. From the practical viewpoint of polymer processes, in order for the catalysts to be used in the prevailing slurry or gas phase processes, it is necessary to modify them to a supported form. In this article, which is based on the above rationale, supported Ziegler-Natta/Metallocene hybrid catalysts were prepared to control the MWD of polyethylene. Hybrid catalysts mean that different catalysts are impregnated on one support [Cho et al., 1998, 1999]. The narrow MWD of polymers produced via the use of metallocene catalysts can be broadened by preparing Ziegler-Natta/Metallocene hybrid catalysts, because of the relatively higher molecular weight of polymers derived from the Ziegler-Natta component. In addition, hybrid catalysts can take advantage of the properties of both the metallocene and the Ziegler-Natta catalysts. Also, because of the compatibility with conventional processes, much effort has been paid to impregnating metallocene catalysts on inert supports. In this study, two kinds of inorganic supports, MgCl_2 and SiO_2 , were prepared, and Ziegler-Natta/Metallocene hybrid catalysts were impregnated on each support. MgCl_2 was prepared by the recrystallization method using a methanol as a dissolution material, and SiO_2 was developed by the sol-gel method. SiO_2 was made by the reaction between stable sol ($-\text{Si}-\text{O}^-\text{Na}^+$) and Mg^{2+} cation. These two kinds of supports would be expected to be useful for the impregnation of catalysts and ethylene polymerization.

^{*}To whom correspondence should be addressed.

E-mail: wyl@snu.ac.kr

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EXPERIMENTAL

1. Materials

High purity ethylene and N_2 (Sinyang Gas Products) were purified by sequential passage through columns 5 Å molecular sieves (Kokusan Chem.), and anhydrous P_2O_5 (Yakuri Chem.). Toluene (Oriental Chem.) as a solvent was purified by distillation over sodium metal. Metallocene catalyst, Cp_2ZrCl_2 (Strem Chem.) and Ziegler-Natta catalyst, $TiCl_4$ (Aldrich Chem.) were used without further purification. Both MAO (methylaluminoxane, type 4, Akzo Chem.) and TiBAL (triisobutylaluminum, Aldrich Chem.) were used as a cocatalyst without further purification. In addition, $MgCl_2$ (Aldrich Chem.), colloidal SiO_2 (LUDOX HS-40, Dupont), and CH_3OH (Farnitalia Carlo Erba) were used for the preparation of the support without further purification.

2. Preparation of Recrystallized $MgCl_2$ and Impregnation of Catalysts

0.10 mole (9.52 g) of $MgCl_2$ was introduced into a glass reactor and 100 ml of methanol was added. 100 ml n-decane was then added to this solution and the mixture was stirred at 2,000 rpm under vacuum at 80 °C. This recrystallized magnesium-adduct ($CH_3OH/MgCl_2$) was pretreated with MAO according to the methanol contents, prior to the impregnation of catalysts. MAO-treated supports (2 g) were suspended in 100 ml toluene, and reacted with 0.10 g Cp_2ZrCl_2 at 50 °C for 2 hours (Cp_2ZrCl_2 /MAO/ $CH_3OH/MgCl_2$). 3 ml of $TiCl_4$ was introduced into this catalyst and the mixture was stirred at 70 °C for 2 hours to give the final Ziegler-Natta/Metallocene hybrid catalysts ($TiCl_4/Cp_2ZrCl_2$ /MAO/ $CH_3OH/MgCl_2$).

3. Preparation of Bisupport ($MgCl_2/SiO_2$) and Impregnation of Catalysts

$MgCl_2$ was introduced into a reactor and distilled water was added. $MgCl_2$ solution was then introduced into a corn oil media. It was uniformly dispersed at a rate of 1,000 rpm and then colloidal SiO_2 was added to initiate gelation. The agglomerated particles were separated, washed, and dried at 80 °C for 24 hours. Bisupport ($MgCl_2/SiO_2$) was suspended in toluene and MAO was added dropwise according to hydroxyl content. This mixture was washed and dried in vacuum. The dried 2 g of bisupport was suspended in 100 ml of toluene and reacted with 0.10 g Cp_2ZrCl_2 at 50 °C for 2 hours and then washed (Cp_2ZrCl_2 /MAO/ $MgCl_2/SiO_2$). This catalyst was followed by the reaction with 3 ml of $TiCl_4$ at 70 °C for 2 hours to give a hybrid catalyst ($TiCl_4/Cp_2ZrCl_2$ /MAO/ $MgCl_2/SiO_2$).

4. Characterization and Ethylene Polymerization

To determine the methanol and hydroxyl contents, TGA (Perkin-Elmer, TGA7) was used. The elemental contents were measured by using ICP (VG PQ2-Turbo, VG). DSC (V4.0 B Dupont) was carried out at a rate of 10 °C/min. Mw and MWD of polymer were measured by GPC (PL-210, Polymer Laboratory) at 160 °C. 300 ml of toluene and cocatalyst (MAO or TiBAL) were introduced into a 1 L glass reactor under a stream of N_2 and then evacuated to remove N_2 . Ethylene was then fed at a constant pressure of 1.3 bar containing a hydrogen partial pressure of 0.2 bar. The polymerization was initiated by introducing the catalyst suspension into the reactor with a syringe at 70 °C. After 50 min, polymerization was terminated by the addition of hy-

drochloric acid solution in methanol.

RESULTS AND DISCUSSION

1. Characteristics of Recrystallized $MgCl_2$ and Impregnation of Catalysts

In the recrystallized $MgCl_2$ ($CH_3OH/MgCl_2$), a considerable amount of methanol (ca. 50 wt%) exists. Since the methanol in the support acts as a deactivation material, that is, Lewis base, for the metallocene catalysts, it should be eliminated or reduced to the lowest possible level. One method is to heat a support physically under N_2 atmosphere to reduce the methanol content. The other method involves a chemical reaction between the methanol in the support and the alkylaluminum compounds such as TiBAL and MAO. The first method is not proper for the impregnation of metallocene catalysts, because after the thermal pretreatment, the methanol in the support changes into methoxy groups, which do not serve as impregnation sites for the metallocene catalysts. Cho et al. [1998] showed that metallocene catalyst was impregnated at the sites where methanol and alkylaluminum compounds reacted. Therefore, stoichiometric amount of MAO was used to eliminate the methanol in the support and then Cp_2ZrCl_2 was impregnated.

Table 1 shows the elemental analysis of catalysts. Different from the results in a previous paper [Cho et al., 1998], Cp_2ZrCl_2 was not well impregnated on the MAO-treated support, quite different from the TiBAL-treated one. It is conceivable that the bulky size of MAO doesn't well impregnate the metallocene catalyst compared with the relatively small size of TiBAL. For the hybrid catalysts, the impregnation contents of the Ziegler-Natta catalyst were higher than those of the metallocene catalyst.

2. Characteristics of Bisupport ($MgCl_2/SiO_2$) and Impregnation of Catalysts

Fig. 1 shows a plausible mechanism for the formation of bisupport. The colloidal SiO_2 used in the preparation of bisupport is about 12 nm in diameter. Since these particles have negative

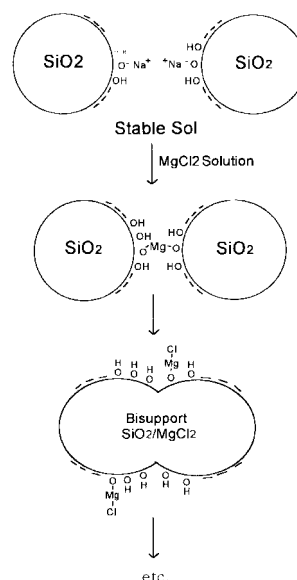


Fig. 1. Plausible mechanism of the reaction between colloidal SiO_2 and $MgCl_2$ solution.

charges on their surfaces, repulsive forces between particles suppress the agglomeration of particles. If MgCl_2 solution is added to this stable sol, gelation occurs by the reaction between the surface anion of colloidal silica and the dissolved magnesium cation.

On the surface of the bisupport, the hydroxyl groups ($-\text{Si}-\text{OH}$) coexist with the magnesium oxide complexes ($-\text{Si}-\text{O}-\text{Mg}-\text{Cl}$), which were produced by the reaction between the magnesium dichloride and the hydroxyl groups. These two sites competitively serve the impregnation sites of catalysts. Cho et al. [1999] showed that the impregnation contents of Cp_2ZrCl_2 increased with the increase of the contents of magnesium oxide complexes on the surface. This means that the impregnation sites on the bisupport are mainly outer surface and that magnesium oxide complexes ($-\text{Si}-\text{O}-\text{Mg}-\text{Cl}$) on the surface of support play a role for the impregnation precursor. As shown in Table 1, similar to the result of the hybrid catalysts supported on the recrystallized MgCl_2 , the impregnation level of TiCl_4 was higher than that of Cp_2ZrCl_2 .

3. Ethylene Polymerization over Hybrid Catalysts

Tables 2 and 3 show the results of ethylene polymerization

over the metallocene supported catalyst ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{Support}$), the hybrid catalysts ($\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{Support}$), and the Ziegler-Natta supported catalyst ($\text{TiCl}_4/\text{MAO}/\text{Support}$). In comparing the activities of the metallocene supported catalyst with those of the Ziegler-Natta supported catalyst, the activity tends to decrease in an orderly manner due to the relatively low activity characteristics of the Ziegler-Natta catalyst.

The polymer produced via the hybrid catalysts with MAO cocatalyst showed different patterns. The polymers produced via the hybrid catalysts supported on the recrystallized MgCl_2 showed one melting temperature (T_m), which was mainly polymerized by the Ziegler-Natta component, as shown in Fig. 2. In contrast to this pattern, the polymer produced via the hybrid catalysts supported on the bisupport ($\text{MgCl}_2/\text{SiO}_2$) showed two T_m , as shown in Fig. 3. In this case, the polymer portion produced by the metallocene catalyst is more dominant than that by the Ziegler-Natta catalyst. This is due to the higher activity of the Ziegler-Natta catalyst vis-à-vis that of the metallocene catalyst over the recrystallized MgCl_2 , and that the activity of the metallocene catalyst is more active vis-à-vis that of the Ziegler-Natta catalyst over the bisupport.

As shown in Fig. 4, the GPC profiles of polymers produced by the MgCl_2 -supported catalysts show the same tendency to the DSC thermograms. Although, the GPC profile of the polymer produced via the hybrid catalysts shows monomodality, the MWD was broadened compared that of polymer produced via the Ziegler-Natta catalyst. For the case of the hybrid catalysts supported on bisupport ($\text{MgCl}_2/\text{SiO}_2$), the modality could be changed by using two cocatalysts, both TiBAL and MAO, as shown in Fig. 5. With the increase of cocatalyst ratio, TiBAL to MAO, the peak

Table 1. Elemental analysis of the supported catalysts

Catalysts	Al (wt%)	Zr (wt%)	Ti (wt%)
$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$	1.30	0.10	-
$\text{TiCl}_4/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$	2.71	-	0.70
$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$	1.92	0.06	0.71
$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$	10.9	0.14	-
$\text{TiCl}_4/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$	11.2	-	2.78
$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$	9.98	0.12	2.30

Table 2. Analytical data on the polyethylene produced via various catalysts supported on recrystallized MgCl_2

Catalysts	Cocatalyst	Mole ratio (Al/[Metal])	Activity ^a	T_m (°C)	Xc ^b (%)	Mw (10^{-5})	MWD
$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$	MAO	Al/Zr=3000	38.8	129.5	70.8	0.48	3.8
$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$	MAO	Al/Zr=3000	6.21	137.0	57.2	6.40	8.6
	MAO	Al/Zr=3000	11.4	137.1	60.2	6.09	7.4
	TiBAL	Al/Ti=25					
	MAO	Al/Zr=3000	11.3	137.2	60.8	5.60	6.1
	TiBAL	Al/Ti=50					
$\text{TiCl}_4/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$	TiBAL	Al/Ti=100	9.1	137.3	59.8	5.88	6.4
	TiBAL	Al/Ti=100	12.5	137.3	61.4	5.45	5.9

^aActivity: kg-HDPE/g-[Metal]·atm·hr. ^bCrystallinity: $X_c(\%) = 100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^* = 282.84$ J/g.

Table 3. Analytical data on the polyethylene produced via various catalysts supported on bisupport ($\text{MgCl}_2/\text{SiO}_2$)

Catalysts	Cocatalyst	Mole ratio (Al/[Metal])	Activity ^a	T_m (°C)	Xc ^b (%)	Mw (10^{-5})	MWD
$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$	MAO	Al/Zr=3000	20.2	131.0	60.1	0.51	2.3
$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$	MAO	Al/Zr=3000	4.43	131.0	59.6	2.10	3.6
				137.8			
	MAO	Al/Zr=3000	3.58	128.3	44.3	5.84	8.1
	TiBAL	Al/Ti=100		139.5			
	MAO	Al/Zr=3000	2.92	127.9	40.4	8.33	42.0
	TiBAL	Al/Ti=300		139.5			
	TiBAL	Al/Ti=100	2.50	139.7	39.8	7.34	5.9
$\text{TiCl}_4/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$	TiBAL	Al/Ti=100	1.97	139.0	42.5	7.60	6.3

^aActivity: kg-HDPE/g-[Metal]·atm·hr. ^bCrystallinity: $X_c(\%) = 100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^* = 282.84$ J/g.

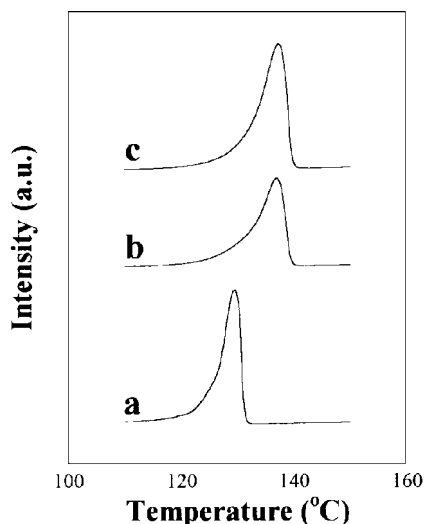


Fig. 2. DSC thermograms of polyethylene produced via various catalysts supported on recrystallized MgCl_2 .

(a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$, MAO (Al/Zr=3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$, MAO (Al/Zr=3000); (c) $\text{TiCl}_4/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$, TiBAL (Al/Ti=100).

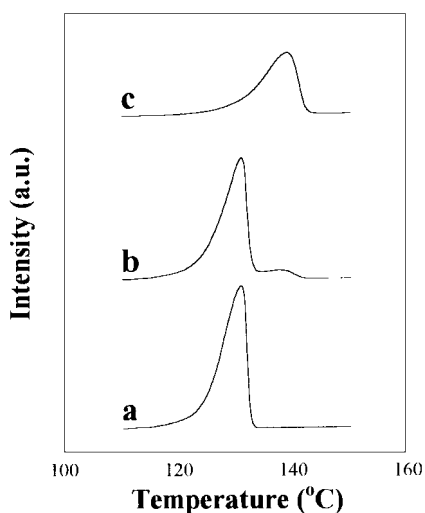


Fig. 3. DSC thermograms of polyethylene produced via various catalysts supported on bisupport ($\text{MgCl}_2/\text{SiO}_2$).

(a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$, MAO (Al/Zr=3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$, MAO (Al/Zr=3000); (c) $\text{TiCl}_4/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$, TiBAL (Al/Ti=100).

intensity around 140 °C corresponding to TiCl_4 increased. Also, the peak around 130 °C corresponding to Cp_2ZrCl_2 decreased with increasing amounts of TiBAL. This is due to the fact that aluminum alkyls form complexes with the active zirconium, occupy the vacant coordinate sites, and finally reduce the active sites of the metallocene catalyst [Fischer et al., 1993].

This result also suggests that the resulting polymer blends are composed of two lamella structures, each of which are polymerized by one of the catalysts. GPC analyses indicate that the Mw increases from the metallocene to the hybrid catalysts because of the characteristics of Ziegler-Natta catalyst. It is especially noteworthy that the Mw and the MWD via the hybrid catalysts were high, broad and controllable with the variation of cocatalyst ratio.

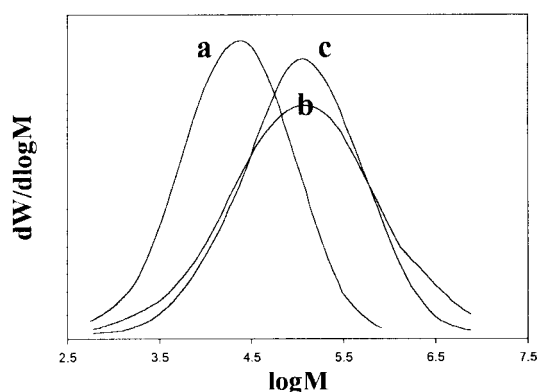


Fig. 4. GPC profiles of polyethylene produced via various catalysts supported on recrystallized MgCl_2 .

(a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$, MAO (Al/Zr=3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$, MAO (Al/Zr=3000); (c) $\text{TiCl}_4/\text{MAO}/\text{CH}_3\text{OH}/\text{MgCl}_2$, TiBAL (Al/Ti=100).

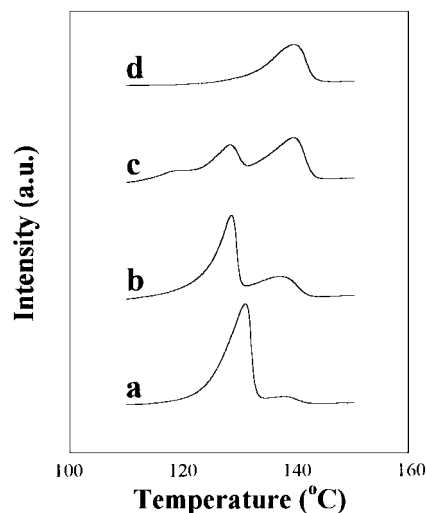


Fig. 5. DSC thermograms of polyethylene produced via hybrid catalysts supported on bisupport ($\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$).

(a) MAO (Al/Zr=3000); (b) MAO & TiBAL (Al/Ti=100); (c) MAO & TiBAL (Al/Ti=300); (d) TiBAL (Al/Ti=100).

Similar to the DSC thermograms, the GPC curves showed bimodal patterns, as shown in Fig. 6. Consequently, the hybrid catalysts are capable of producing a blend of polyethylenes, and there is no strong chemical interaction between the two catalysts.

CONCLUSIONS

Hybrid catalysts appear to be compatible on the supports and produce a blend of polymers, suggesting that the hybrid catalysts acted as individual active species on support. Mw and MWD of polymer produced by the hybrid catalysts showed a high Mw and a broad MWD. However, the modality patterns differ with the type of support, and, for the case of the hybrid catalyst over bisupport, the modality pattern can be varied with the TiBAL to MAO cocatalyst ratio. Especially, the Mw and the MWD of polymer can be controllable by adjusting the mole ratio of cocatalysts.

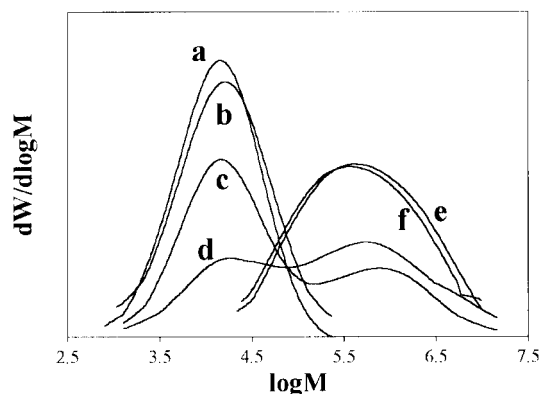


Fig. 6. GPC profiles of polyethylene produced via various catalysts supported on bisupport ($\text{MgCl}_2/\text{SiO}_2$).

(a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$, MAO ($\text{Al}/\text{Zr}=3000$); $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$; (b) MAO ($\text{Al}/\text{Zr}=3000$); (c) MAO & TiBAL ($\text{Al}/\text{Ti}=100$); (d) MAO & TiBAL ($\text{Al}/\text{Ti}=300$); (e) TiBAL ($\text{Al}/\text{Ti}=100$); (f) $\text{TiCl}_4/\text{MAO}/\text{MgCl}_2/\text{SiO}_2$, TiBAL ($\text{Al}/\text{Ti}=100$).

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