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Characteristics of ethylene polymerization over Ziegler–Natta/metallocene catalysts Comparison between hybrid and mixed catalysts

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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 the sol–gel method, respectively. The polyethylene produced by the Ziegler–Natta/metallocene hybrid and mixed catalysts showed two melting temperatures and a bimodal MWD corresponding to products arising from each of the individual catalysts. This suggests that these Ziegler–Natta/metallocene catalysts acted as individual active species, and as a result, produced a blend of polymers. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ethylene polymerization; Ziegler–Natta/metallocene catalysts; Hybrid catalyst; Mixed catalyst

1. Introduction

In polymer processing, the molecular weight (MW) and the molecular weight distribution (MWD) represent basic properties, which serve as major determinants of polymer properties. The MW largely relates to the determinant of mechanical properties, while MWD is largely responsible for rheological properties. High MW polymer has not only improved physical properties but also is difficult to process. On the other hand, an increase in MWD tends to improve flowability at high shear rate, which is important for blowing and extrusion techniques [1,2]. Therefore, it is necessary to control the MW as well as the MWD of polymers in order to optimize both the mechanical and the rheological properties.

Several methods for controlling the MW and the MWD of polymers are available. The first method involves physically blending the polymers of different average MW. However, polymer blends have high gel levels, and as a result, miscibility problems can occur. The second method involves the use of a series of reactors, each of which involves different polymerization conditions, such as temperature and pressure. This method is unacceptable because it involves additional processes, thus increasing capital costs. The third method is to combine two or more catalysts in a single reactor, thus producing polymers with different MW ranges. In this case, a highly advanced catalyst technology is required. Most studies in this area have dealt with the use of catalyst mixtures which are homogeneous [3,4]. However, a limited number of reports have been published which deal with MWD in heterogeneous catalysts. 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 heterogeneous form.

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In this study, which is based on the above rationale, heterogeneous Ziegler–Natta/metallocene hybrid and mixed catalysts were prepared in order to control the MWD of polyethylene. In this case, which is different from other methods, hybrid catalysts were investigated in order to control the MWD of polymers by impregnating both the Ziegler–Natta and metallocene catalysts into one support.

It is conceivable that polymer blends of a low MW polymer produced by a metallocene catalyst and a high MW polymer by a Ziegler–Natta catalyst affect the MWD and MW. In addition, two types of inorganic supports, $MgCl_2$ and SiO_2, for the impregnation of catalysts were prepared by the recrystallization and the sol–gel method, respectively. These two types of supports were used for the impregnation of catalysts and ethylene polymerization was performed in order to investigate the characteristics of the catalysts.

2. Experimental

2.1. Materials

Ethylene and N_2 (Sinyang Gas Products) were purified by sequential passage through columns containing 5 Å molecular sieves and anhydrous P_2O_5 (Yakuri Chem.). Toluene (Oriental Chem.) was purified by distillation over Na. $MgCl_2$ (Aldrich Chem.), CH_3OH (Carlo Erba.), *n*-decane (Aldrich Chem.), colloidal SiO_2 (LUDOX HS-40, Dupont), Cp_2ZrCl_2 (Strem Chem.), $TiCl_4$ (Aldrich Chem.), triisobutylaluminum (TiBAL; Aldrich Chem.), and methylaluminoxane (MAO; type 4, Akzo Chem.) were used without further purification.

2.2. Preparation of $MgCl_2$ by the recrystallization method and catalyst impregnation

$MgCl_2$ of 0.10 mol was introduced into a reactor and 100 ml of methanol was then added. *n*-Decane of 100 ml was then added to this solution and the mixture was stirred at 2000 rpm under vacuum at 80°C. This recrystallized support ($MgCl_2 \cdot 4CH_3OH$) was pretreated with TiBAL according to the methanol content (18 mmol/g-support). Two grams of the TiBAL-treated supports reacted with 0.10 g of Cp_2ZrCl_2 dissolved in 100 ml of toluene at 50°C for 2 h (Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$, Zr: 1.03 wt.%). $TiCl_4$ of 3 ml was then introduced to this supported catalyst. The mixture was stirred at 70°C for 2 h, and washed nine times with 100 ml of toluene, and then dried under vacuum ($TiCl_4$/Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$, Zr: 0.87 wt.%, Ti: 2.47 wt.%). Two grams of the TiBAL-treated supports were suspended in 100 ml of toluene, and reacted with 3 ml of $TiCl_4$ at 70°C for 2 h and then washed in the same manner ($TiCl_4$/TiBAL/$MgCl_2 \cdot 4CH_3OH$, Ti: 2.88 wt.%).

2.3. Preparation of SiO_2 by the sol–gel method and catalyst impregnation

$MgCl_2$ of 0.035 mol was dissolved in 20 ml of distilled water (pH 6.70), and was then suspended in 1.4 l of corn oil media. It was uniformly dispersed and 80 ml of colloidal SiO_2 (0.692 mol of Si) was then added to initiate gelation. The particles were separated, washed with toluene, and dried at 80°C for 24 h. The support (SiO_2) was suspended in 100 ml of toluene and MAO was added according to the hydroxyl content (10 mmol/g-support). Two grams of the MAO-treated support reacted with 0.10 g of Cp_2ZrCl_2 dissolved in 100 ml of toluene at 50°C for 2 h (Cp_2ZrCl_2/MAO/SiO_2, Zr: 0.10 wt.%). This catalyst was reacted with 3 ml of $TiCl_4$ at 70°C for 2 h, and washed nine times with 100 ml of toluene, and then dried under vacuum ($TiCl_4$/Cp_2ZrCl_2/MAO/SiO_2, Zr: 0.06 wt.%, Ti: 0.71 wt.%). Two grams of the MAO-treated supports were suspended in 100 ml toluene, and reacted with 3 ml of $TiCl_4$ at 70°C for 2 h and then washed in the same manner ($TiCl_4$/MAO/SiO_2, Ti: 0.70 wt.%).

2.4. Characterization and polymerization of ethylene

The Zr and Ti contents were determined by ICP (VG PQ2-Turbo). The methanol content of the recrystallized $MgCl_2$ was determined by TGA (Perkin-Elmer, TGA7). The morphology of the support and the relative elemental surface ratios of Si:Mg:Cl on the support were measured by SEM and SEM-EDS (JSM-840A, JEOL). The surface area was determined with an N_2-BET analyzer (ASAP-2000, Micromeritics). An analysis by DSC (V 4.0B, Dupont) was carried out and recorded for the first run at a heating rate of 10°C/min. MW and the MWD were determined by GPC (PL-210, Polymer Laboratory) at 160°C using 1,2,4-trichlorobenzene as a solvent.

Three hundred milliliter of toluene and cocatalyst were introduced into a 1 l glass reactor equipped with a magnetic stirrer under a stream of N_2 and the reactor was then evacuated to remove the N_2. Hydrogen of 0.2 bar was fed into the reactor prior to the introduction of ethylene, and ethylene was then fed into the reactor at a constant pressure of 1.3 bar. The polymerization reaction was initiated at 70°C by introducing the catalyst suspension into the reactor with a syringe. The reaction was terminated after 50 min by the addition of an excess of dilute hydrochloric acid solution in methanol, and the resulting polymer was isolated, dried, and characterized.

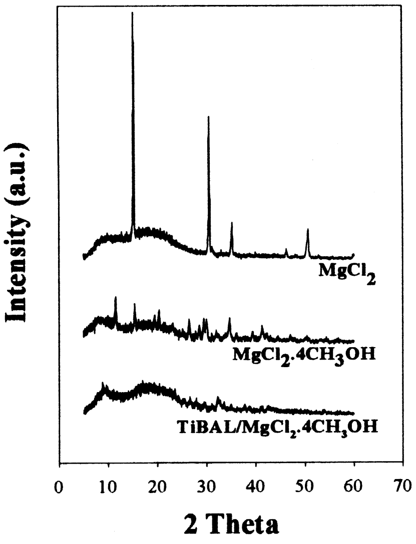

Fig. 1. XRD patterns of the recystallized $MgCl_2$.

3. Results and discussion

3.1. Characteristics of recrystallized $MgCl_2$ and the impregnation of catalysts

Anhydrous $MgCl_2$ has a cubic close packing (c.c.p.) structure which gives a strong XRD pattern at $2\theta = 15°$ (0 0 3), 35° (0 0 4) and 50° (1 1 0 plane) [5]. However, the peak intensities of the recrystallized $MgCl_2$ were weaker compared with those of anhydrous $MgCl_2$ as shown in Fig. 1, suggesting that $MgCl_2 \cdot n CH_3OH$ was formed. The approximate value of n is 4, based on the calculated methanol content (ca. 56.5 wt.%), as evidenced by TGA analysis. When these supports were treated with TiBAL, the peaks disappeared as a result of the removal of methanol in the form of aluminum methoxide species, which arose via the reaction of TiBAL with methanol in the support. These aluminum methoxides are important because these chemical complexes create the impregnation sites for the metallocene catalysts. The results in Table 1 show that the impregnation contents of Cp_2ZrCl_2 increased with increasing levels of TiBAL pretreatment, and that the surface area of catalyst drastically increased as well.

To evaluate the influence of methanol in the support on the impregnation of Cp_2ZrCl_2, the supports were thermally pretreated at 100 and 200°C, respectively, followed by the reaction with TiBAL, based on the residual methanol content. In this case, however, a small amount of Cp_2ZrCl_2 was impregnated. This is due to the fact that the methanol in the support was converted to methoxy groups, which do not serve as the impregnation sites, as shown in Eq. (1) [6]. Conse-

Table 1
Characteristics of the recrystallized $MgCl_2$ and catalysts

Supports and catalysts	Surface area (m^2/g)	TiBAL treatment (mol/l)	Zr (wt.%)	Ti (wt.%)
Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$-100°C	42.3	0.3	0.012	–
Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$-200°C	39.8	0.2	–	–
Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$	382.1	0.6	1.03	–
	209.4	0.3	0.43	–
	68.3	0.15	–	–
$TiCl_4$/Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$	428.5	0.6	0.87	2.47
$TiCl_4$/TiBAL/$MgCl_2 \cdot 4CH_3OH$	412.7	0.6	–	2.88

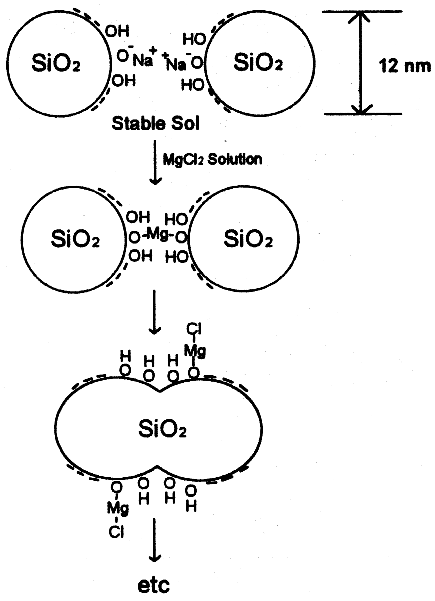

Fig. 2. Proposed mechanism of the silica support.

quently, it should be noted that the modification of recrystallized $MgCl_2$ by pretreatment with TiBAL provides for the impregnation of the metallocene catalyst,

$$MgCl_2 \cdot 4CH_3OH \rightarrow MgCl_X(OCH_3)_Y + m\text{HCl} + n\text{CH}_3\text{OH} \quad (m+n=4,\ \ X+Y=2) \qquad (1)$$

3.2. Characteristics of SiO_2 and impregnation of the catalysts

Fig. 2 shows a proposed mechanism for the formation of the support. The particles of the colloidal sol are approximately 12 nm in diameter. These particles contain negative charges on their surfaces, which serve to suppress the gelation of particles. When a $MgCl_2$ solution is added to this stable sol, the dissolved magnesium salt neutralizes the negative charges on the surface of the stable sol and the silica undergoes gelation via dimerization, trimerization and further polymerization.

Since the supports are formed in a dispersed medium, particle growth is limited, resulting in the formation of solid particles within a few minutes. As shown in Fig. 3, the support has a spherical morphology and the particle size varies as a function of agitation speed. Table 2 shows the characteristics of the support. The different relative weight ratio of Mg/Si between in the bulk and on the surface of the support was about 50 (w/w), suggesting that magnesium is reasonably well distributed throughout the interior and exterior portions of the supports. In addition, the relative mole ratio of Si:Mg:Cl on the surface of the support indicates that hydroxyl groups on the surface of colloidal silica interact with Mg^{2+} during the formation of the support, thus generating magnesium oxide complexes (–Si–O–Mg–Cl).

3.3. Characteristics of ethylene polymerization over hybrid and mixed catalysts

Tables 3 and 4 show the results of the ethylene polymerization reactions. The melting temperature of the polymer produced by the metallocene catalyst was approximately 130°C, while for the Ziegler–Natta catalyst, it was approximately 135 or 140°C. Since

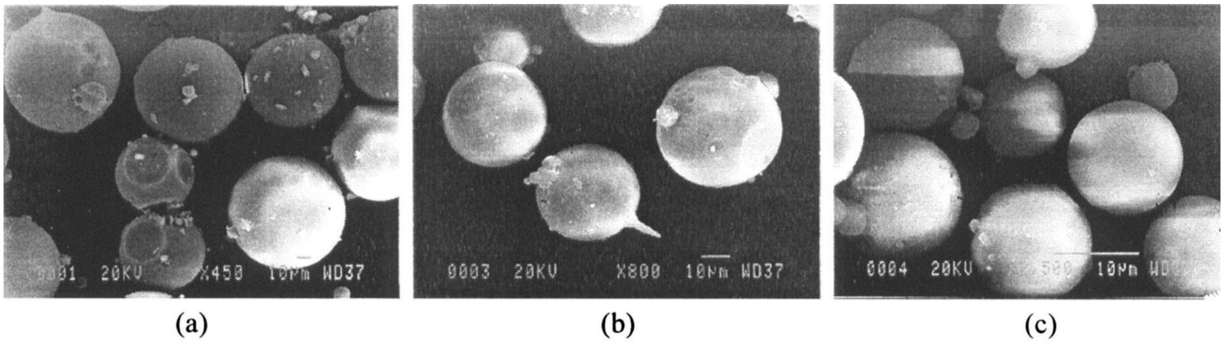

Fig. 3. SEM photographs of the support with respect to the agitation speed: (a) 1000 rpm; (b) 2000 rpm; (c) 3000 rpm.

Table 2
Characteristics of the support with respect to agitation speed

Agitation speed (rpm)	Average particle size (μm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Si, Mg contents in support (wt.%)	Surface ratio Si:Mg:Cl (wt.%)
1000	61.7	138	0.229	Si: 43.1, Mg: 1.34	89.1:1.3:9.6
2000	39.6	135	0.217	Si: 43.9, Mg: 1.47	89.4:1.7:8.9
3000	13.5	134	0.238	Si: 44.5, Mg: 1.39	87.2:1.7:11.1

the hybrid catalysts have two different active sites, the polymers produced via the hybrid catalysts with MAO cocatalyst are represented by two DSC melting peaks, resulting from catalysis by Cp_2ZrCl_2 and $TiCl_4$, respectively. However, the bimodality patterns over the hybrid catalysts are different, as shown in Figs. 4 and 5. For the hybrid catalysts supported on the recrystallized $MgCl_2$ with the MAO cocatalyst, the polyethylene portion produced by the Ziegler–Natta catalyst is more dominant than that produced via the metallocene catalyst. In contrast to this pattern, for the hybrid catalysts supported on SiO_2 with the MAO cocatalyst, the polyethylene 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 SiO_2. For the case of the hybrid catalysts supported on SiO_2, the bimodality could be adjusted by using two cocatalysts, MAO and TiBAL. As shown in Fig. 6, two characteristic peaks, representing the melting points of the polyethylene species resulting from each $TiCl_4$ and Cp_2ZrCl_2 were clearly observed. The peak around 140°C increased with increasing amounts of TiBAL. On the contrary, the peak around 130°C decreased with increasing amounts of TiBAL. This is

Table 3
Analytical data on polyethylene via various catalysts supported on $MgCl_2 \cdot 4CH_3OH$

Catalysts	Cocatalyst	Mole ratio (Al/[metal])	Activity[a]	T_m (°C)	Xc[b] (%)	MW ($\times 10^{-5}$)	MWD
Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$	MAO	Al/Zr = 3000	2535.7	127.8	73.8	0.46	3.4
$TiCl_4$/Cp_2ZrCl_2/TiBAL/$MgCl_2 \cdot 4CH_3OH$	MAO	Al/Zr = 3000	15720.6	126.4/135.3	68.9	6.81	9.7
$TiCl_4$/TiBAL/$MgCl_2 \cdot 4CH_3OH$	TEA	Al/Ti = 300	923.4	134.9	62.0	7.80	6.0

[a] Activity: kg-HDPE/mol-[metal] atm h.
[b] Crystallinity: Xc (%) = $100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^* = 282.84$ J/g.

Table 4
Analytical data on polyethylene via various catalysts supported on SiO_2

Catalysts	Cocatalyst	Mole ratio (Al/[metal])	Activity[a]	T_m (°C)	Xc[b] (%)	MW ($\times 10^{-5}$)	MWD
Cp_2ZrCl_2/MAO/SiO_2	MAO	Al/Zr = 3000	1842.6	131.0	60.1	0.51	2.3
$TiCl_4$/Cp_2ZrCl_2/MAO/SiO_2	MAO	Al/Zr = 3000	616.3	131.0/137.8	59.6	2.10	3.6
	MAO TiBAL	Al/Zr = 3000 Al/Ti = 100	498.0	128.3/139.5	44.3	5.84	8.1
	MAO TiBAL	Al/Zr = 3000 Al/Ti = 300	406.2	127.9/139.5	40.4	8.33	42.0
	TiBAL	Al/Ti = 100	119.8	139.7	39.8	7.34	5.9
$TiCl_4$/MAO/SiO_2	TiBAL	Al/Ti = 100	94.4	139.0	42.5	7.60	6.3

[a] Activity: kg-HDPE/mol-[metal] atm h.
[b] Crystallinity: Xc (%) = $100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^* = 282.84$ J/g.

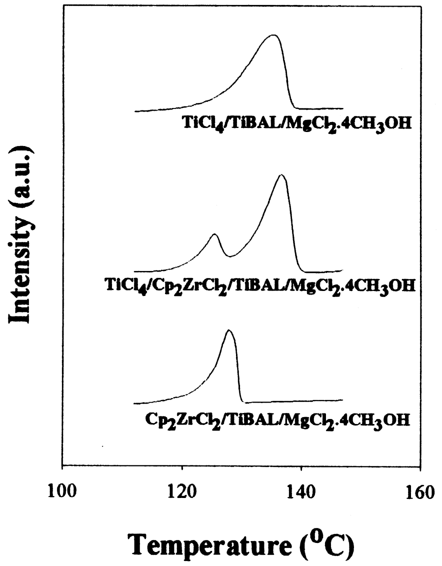

Fig. 4. DSC thermograms of the polyethylene by $MgCl_2$-supported catalysts.

due to the fact that alkylaluminum compounds act as selective poison for the metallocene catalyst because aluminum alkyls form alkyl aluminum chloride complexes with the active zirconocene species, and as a result, the amount of active zirconocene is reduced [7].

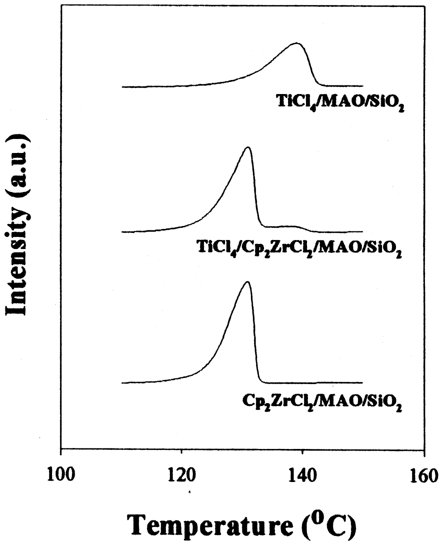

Fig. 5. DSC thermograms of the polyethylene by SiO_2 supported catalysts.

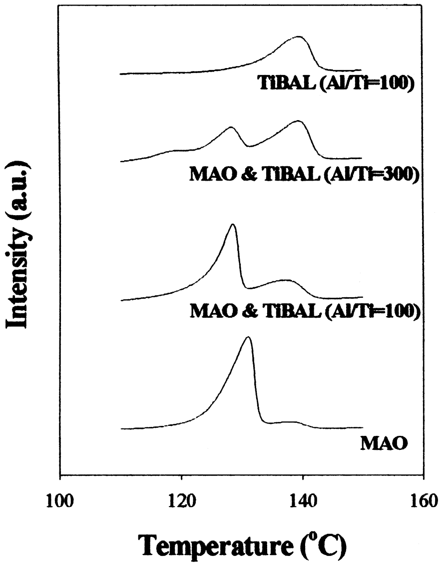

Fig. 6. DSC thermograms of the polyethylene by $TiCl_4/Cp_2ZrCl_2/MAO/SiO_2$ catalysts.

The variation of GPC profiles is similar to that of DSC thermograms as shown in Fig. 7. The positions of the two peaks via the hybrid catalysts are consistent with those of the polymers produced by metallocene and Ziegler–Natta catalysts, respectively. It is noteworthy that this variation in modality affects the MW as well as the MWD, and can be controlled by varying the cocatalyst ratio. In addition, the MW and the MWD can be controlled by the use of the

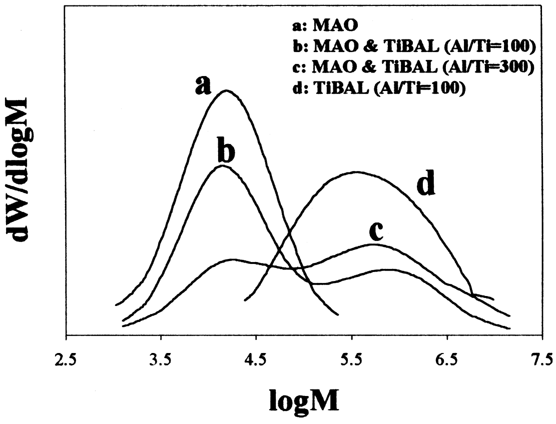

Fig. 7. GPC profiles of the polyethylene by $TiCl_4/Cp_2ZrCl_2/MAO/SiO_2$ catalysts.

Table 5
Analytical data on the polyethylene produced by mixed catalysts with respect to Ti/Zr ratio: $Cp_2ZrCl_2/MAO/SiO_2$ and $TiCl_4/TiBAL/MgCl_2 \cdot 4CH_3OH$

Ti/Zr (mol/mol)	Cocatalyst (MAO)	Activity[a]	T_m (°C)	Xc[b] (%)	MW ($\times 10^{-5}$)	MWD
1/–	Al/Ti = 2000	7996.3	137.8	64.5	8.25	6.5
1/5	Al/[Zr + Ti] = 2000	7610.7	130.0/137.7	68.6	6.74	13.8
1/10	Al/[Zr + Ti] = 2000	6789.1	129.5/136.2	70.1	4.58	11.9
1/20	Al/[Zr + Ti] = 2000	4563.3	129.8/135.2	69.7	2.77	7.7
–/1	Al/Zr = 2000	2214.9	128.9	75.3	0.52	2.7

[a] Activity: kg-HDPE/mol-[metal] atm h.

[b] Crystallinity: Xc (%) = $100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^* = 282.84$ J/g.

Ziegler–Natta/metallocene mixed catalysts. Table 5 shows the results for the polymers produced using the mixed catalysts. With the MAO cocatalyst, both the metallocene and the Ziegler–Natta supported catalyst are active, and in this case, the bimodality can be varied with the mole ratio of catalysts, Cp_2ZrCl_2–$TiCl_4$. The MW increases with increasing the mole ratio of $TiCl_4$–Cp_2ZrCl_2 due to the higher MW produced by $TiCl_4$, and the MWD varies with respect to the variation in the modality. As shown in Figs. 8 and 9, the portion of polyethylene produced by the Ziegler–Natta catalyst increases with increasing levels of $TiCl_4$, and the variation of peak intensity in GPC showed the same tendency in the DSC thermograms.

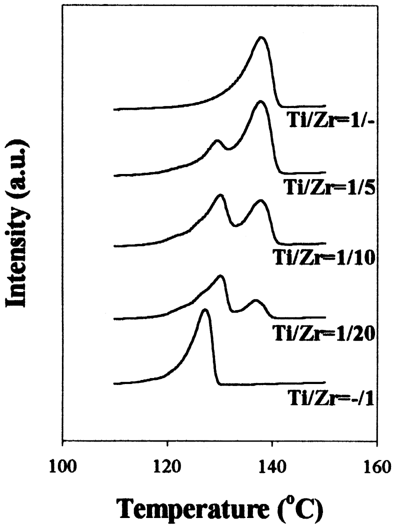

Fig. 8. DSC thermograms of the polyethylene with mixed catalysts with respect to Ti/Zr.

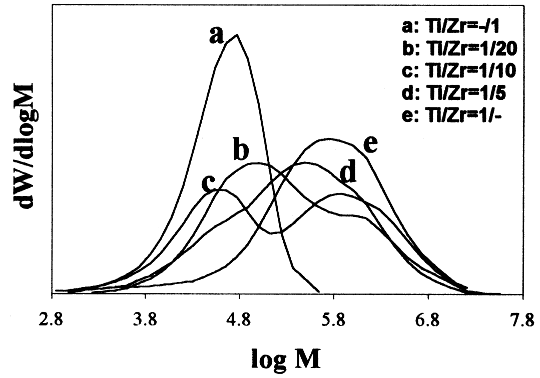

Fig. 9. GPC profiles of the polyethylene with mixed catalysts with respect to Ti/Zr ratio.

4. Conclusions

Hybrid catalysts appear to be compatible on the supports, and produce a blend of polymers. The resulting polymers showed bimodal patterns, as evidenced by DSC and GPC analyses, suggesting that the hybrid catalysts acted as individual active species over the support. However, the bimodality patterns differ with the type of support, and for the case of hybrid catalysts over SiO_2, the bimodality patterns can be varied with the TiBAL–MAO cocatalyst ratio. In addition, the mixed catalysts are capable of producing a blend of polymers, and the MW and MWD can be controlled by varying the catalyst ratio, Cp_2ZrCl_2–$TiCl_4$.

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