(Co)polymerization Behavior of Supported Metallocene Catalysts. I. Ligand and Substituent Effect

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ABSTRACT: Ethylene polymerization and its copolymerization with 1-hexene with a set of supported metallocene catalysts were studied. As a carrier, the complex of magnesium chloride with tetrahydrofuran, which was previously pretreated with a triisobutylaluminium (TIBA), was used. The investigated metallocene compound differs in the metal type (Zr or Ti), the nature of the alkyl substituent in the cyclopentadienyl ring, and the type of ligand (Cp or Ind). The effect of catalyst composition on the anchored metal content, catalyst activity, comonomer reactivity, and polymer properties was investigated. The results obtained with supported catalysts were compared with those obtained with their homogeneous counterparts under the same (co)polymerization conditions. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 5562–5570, 2005

Keywords: copolymerization; metallocene catalysts; structure; support

INTRODUCTION

The discovery (by Sinn and Kaminsky) of catalytic systems based on metallocenes and alkylaluminoxane for olefin polymerization initiated a new area of research in the field of Ziegler–Natta catalysis. Initially academic research had focused on homogeneous catalytic systems. The development of a broad series of new metallocene complexes came later; however, this exclusive focus on homogeneous catalytic systems allowed an insight into polymerization mechanism. Although the homogeneous metallocene catalysts offer a lot of unique potentiality, for example, high activity and control of polymer stereoregularity, there are also some problems connected with their industrial application. The most important ones are the inability to use

them in gas-phase or slurry processes and the lack of polymer morphology control. One way of eliminating these disadvantages is the immobilization of metallocene compounds on a support that is similar to the one performed in Ziegler–Natta catalysis. At first glance it seems an easy task; in practice, however, it is very difficult to anchor the metallocene compound to the surface of the carrier without losing its activity, stereochemical control, and the ability to produce a copolymer with statistical comonomer distribution.[1,2]

In the case of homogenous zirconocene catalysts, the strong influence of ligand nature on catalytic properties is well known. However, it should be taken into account that direct comparison of the results obtained by various research groups is either very difficult or impossible because of different experimental conditions (the activity of the catalyst being solvent- and cocatalyst-dependent). The most active are zirconocene dichloride or dialkyl complexes containing indenyl ligands (Ind), followed by cyclopentadienyl (Cp) with the lowest activity shown

with fluorenyl ligands (Flu).[3,4] There are, however, other data showing that metallocene complexes with Cp ligands are more active than catalysts with Ind ones in copolymerization of ethylene with 1-hexene. Both catalytic systems show, however, a very similar ability to incorporate comonomers into polyethylene chain.[5] The molecular weight of polyethylene obtained with the aforementioned catalyst declines in the following order: Flu, Ind, Cp.[3] The impact of alkyl substituents on ligands around a metal centre on rates of polymerization and catalytic activities as well as polymer properties reflects a combination of the steric and electronic effects. Cp ligands that contain donating groups are able to raise catalytic activity in the homo- or copolymerization of ethylene, though it should be noted that the difference in activity between homo- and copolymerization reactions increases as the steric bulk of the catalyst increases (relative copolymerization ability of the catalyst decreases as its bulk increases).[5–7] In the case of 1- and 2-substituted $(R\text{-Ind})_2ZrCl_2$/methylaluminoxane (MAO) catalysts, steric differences offer an explanation for the different polymerization activities between different catalysts.[8]

Although the effect of a coordination sphere on catalyst behavior in olefin polymerization and copolymerization has been widely investigated with homogeneous catalytic systems,[3–16] supported metallocene catalysts are rarely used in these studies, and that too only those supported on silica.[17,18] In the case of silica-supported metallocene catalysts evaluated in ethylene polymerization, dos Santos et al. found that the silica surface played the role of a huge bulky ligand, causing a reduction in catalyst activity. They observed that in some cases the steric effect caused by the support is preponderant over the electronic effect of the ligand substituent.[18] For ethylene/1-hexene copolymerization using similar supported catalysts, it was established that catalyst activities are dependent on electronic effects when n-Bu and Me monosubstituted Cp are compared and on steric effects when comparing n-Bu to i-Bu groups.[17] To our knowledge, this issue has not been explored with respect to metallocene catalysts immobilized on magnesium-type carriers.

In this article, we present the results of studies on the effect of the metal type in metallocene and the coordination sphere around the metallic centre in supported metallocene catalysts on the anchored metal content; catalyst activity in ethylene homo- and copolymerization; comonomer reactivity; and polymer properties as well. The investigated catalysts differ in the nature of the alkyl substituent in the cyclopentadienyl ring, and the type of ligand (Cp or Ind). The supported catalysts were prepared on complex of magnesium chloride with tetrahydrofuran, which was previously pretreated with a triisobutylaluminium (TIBA) to create an appropriate impregnation site. The results obtained with the supported catalysts are compared with those obtained with their homogeneous counterparts under the same (co)polymerization conditions.

EXPERIMENTAL

Materials

All operations were conducted under inert atmosphere (nitrogen), using standard Schlenk and glove box techniques. Metallocenes (Fluka or Aldrich), MAO (Witco, 10.0 wt %), TIBA (Aldrich, 1 M), and anhydrous magnesium chloride (Fluka) were used without further purifications. 1-Hexene (Aldrich), toluene, and tetrahydrofuran (POCh, Poland) were deoxygenated and dried by standard techniques before use. Ethylene (Orlen SA, Poland) and pure nitrogen (Messer) were used after having been passed through a column of sodium metal supported on Al_2O_3. Pure-grade hexane (Orlen SA, Poland) was refined with sulphuric acid, neutralized over a sodium base, rectified, and finally dried by refluxing in argon over sodium metal.

Preparation of Supported Catalysts

The magnesium support was obtained by dissolving magnesium chloride in tetrahydrofuran at room temperature. The complex $MgCl_2(THF)_2$ was precipitated by adding hexane; then it was filtered, washed several times with hexane, and dried. Afterward, the modification of the magnesium complex by TIBA was performed in a manner similar to those reported elsewhere.[19] The supported zirconocene catalysts were prepared by ball-milling $MgCl_2(THF)_2$/TIBA with a metallocene compound in a slurry (toluene), at room temperature for 20 h. Then, the solid was separated from the solution, washed several times with toluene and hexane, and finally dried.
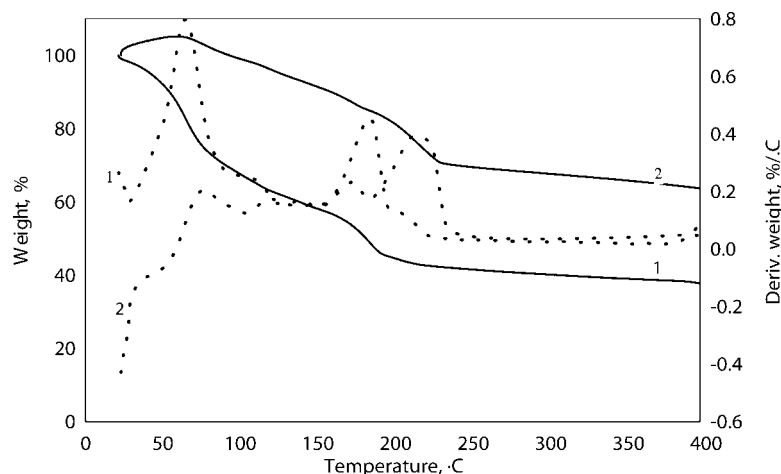
Figure 1. TGA and DTGA thermograms of the MgCl$_2$(THF)$_2$ support (1), and after its modification by TIBA (2).

Polymerization and Copolymerization Procedure

The copolymerization reactions were carried out in a 1-dm^3 reactor equipped with a mechanical stirrer. The reactor was filled with hexane (0.7 dm^3), the required amounts of MAO solution, and 1-hexene (in case of copolymerization) and then the catalyst precursor was charged into the reactor. The (co)polymerization was initiated by the introduction of ethylene. The monomer pressure was kept constant during polymerization by the continuous addition of ethylene (0.5 MPa). The reaction was stopped by the addition of acidic methanol solution. The polymer was subsequently filtered off, washed with methanol, and dried.

Catalyst and (Co)polymer Characterization

The metal content (Zr, Ti, Al, and Mg) of the supported metallocene catalysts was determined by AAS spectroscopy, using a Solaar 969 spectrometer. Molar masses and polydispersity indices (PDI = $\overline{M}_w/\overline{M}_n$) were determined by size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene (0.8 mL/min) as eluent at 142 °C, on a Waters instrument (model 150-C) equipped with a refractive index detector and two columns HT4 (5 × 10^3 – 600 × 10^3) and HT5 (50 × 10^3 – 4 × 10^6). Average molar mass values were calculated from the polystyrene calibration curve obtained with narrow PDI. The heat of fusion (ΔH_f) and the melting temperature (T_m) were measured for samples that had been previously melted and recrystallized using a TA Instruments 2010 DSC calorimeter, at a heating

rate of 5 K/min. From the ΔH_f the percentage crystallinity was calculated: $X_c = \Delta H_f \times (100/290)$.[20] The copolymers' compositions were determined by the modified IR method,[21] using a Philips PU 9800 FTIR spectrometer.

RESULTS AND DISCUSSION

Support Characterization

The presence of THF in the solid magnesium support was evidenced by the presence of peaks at 1036 and 891 cm^{-1} in the FTIR spectrum of MgCl$_2$(THF)$_x$. After modification of the supports by TIBA, the shift of peaks to lower values (1020, 876, and 1010 cm^{-1}, respectively) was observed.

To determine the THF nonmodified magnesium supports, TGA was done. The supports were scanned from 0 to 400 °C by TGA under N$_2$ atmosphere, and the obtained thermograms (Fig. 1) show THF contents around 58 wt %. Examination of the supports by AAS spectro-

Table 1. Metal Loading on a Magnesium Carrier Modified by TIBA

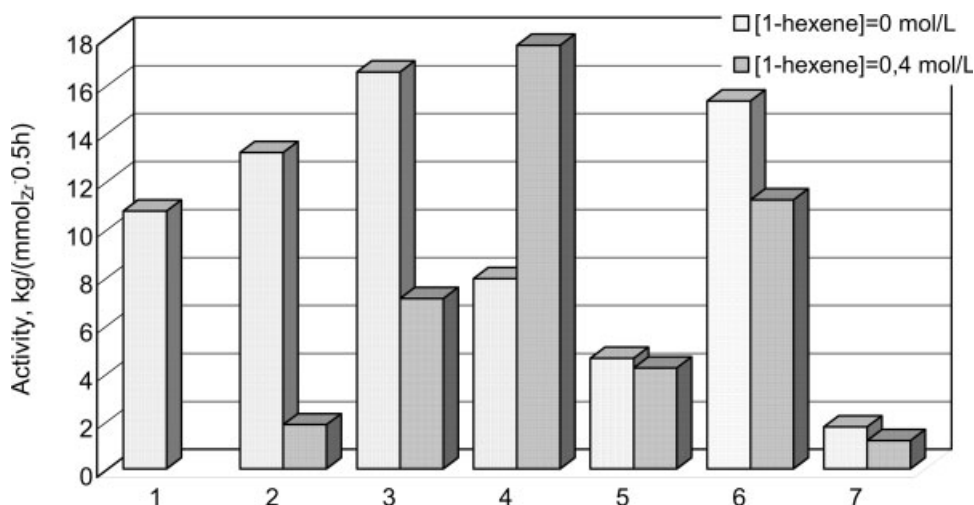| Metallocene	M (wt %)
Cp$_2$ZrCl$_2$	0.22
Cp$_2$TiCl$_2$	0.76
(t-BuCp)$_2$ZrCl$_2$	0.11
(i-PrCp)$_2$ZrCl$_2$	0.06
(n-BuCp)$_2$ZrCl$_2$	0.20
(Me$_5$Cp)$_2$ZrCl$_2$	0.13
Ind$_2$ZrCl$_2$	0.27

M = Ti, Zr.

Figure 2. Catalyst activity of metallocene systems supported on a magnesium carrier in ethylene homopolymerization and ethylene/1-hexene copolymerization: (1)-$(t$-BuCp$)_2$ZrCl$_2$/MAO; (2)-$(n$-BuCp$)_2$ZrCl$_2$/MAO; (3)-$(i$-PrCp$)_2$ZrCl$_2$/MAO; (4)-(Me$_5$Cp$)_2$-ZrCl$_2$/MAO; (5)-Ind$_2$ZrCl$_2$/MAO; (6)-Cp$_2$ZrCl$_2$/MAO; (7)-Cp$_2$TiCl$_2$/MAO. Reaction conditions: cat = 0.07 g, 14 mmol MAO; reaction time: 30 min; temperature: 50 °C.

scopy revealed that 1 g of MgCl$_2$(THF)$_x$ contained 100 mg of Mg. These results correspond with the support chemical formula MgCl$_2$(THF)$_2$.

TGA showed that after modification of magnesium compounds by TIBA the amount of THF in the support decreases to 32 wt % (Fig. 1). The average amount of Al in the catalysts supported on modified magnesium supports was around 15 mg Al/1 g catalyst.

Metal Catalyst Loading

It is well known that the degree of impregnation of metallocene on a support is usually very low, especially when the carrier surface is not modified in any way. To get a higher degree of catalyst loading on the magnesium supports, they were treated, similar to silica-type carriers, with alkylaluminium. The anchored metal content on TIBA-modified magnesium supports for different
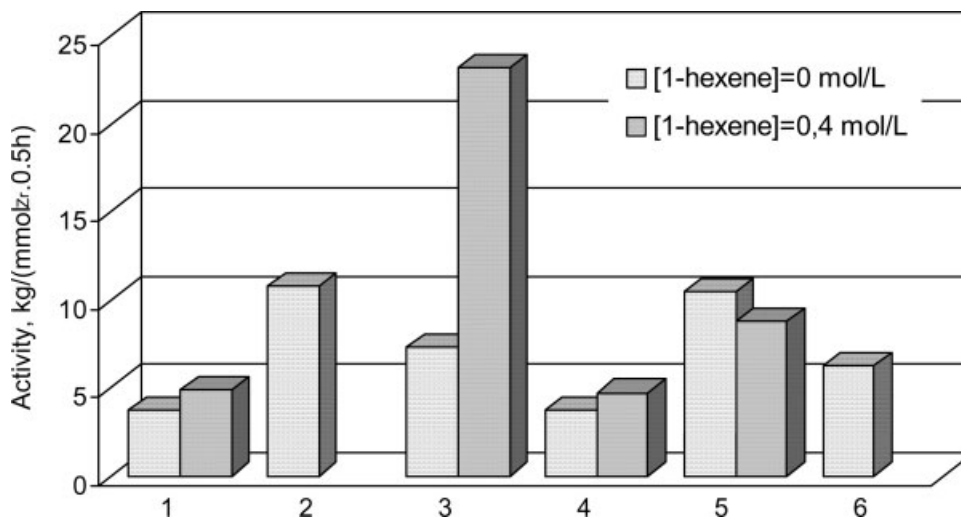

Figure 3. Catalyst activity of homogeneous metallocene systems in ethylene homopolymerization and ethylene/1-hexene copolymerization: (1)-$(t$-BuCp$)_2$ZrCl$_2$/MAO; (2)-$(n$-BuCp$)_2$ZrCl$_2$/MAO; (3)-$(i$-PrCp$)_2$ZrCl$_2$/MAO; (4)-(Me$_5$Cp$)_2$ZrCl$_2$/MAO; (5)-Ind$_2$ZrCl$_2$/MAO; (6)-Cp$_2$ZrCl$_2$/MAO. Reaction conditions: 0.005 mmol Zr, 14 mmol MAO; reaction time: 30 min; temperature: 50 °C.
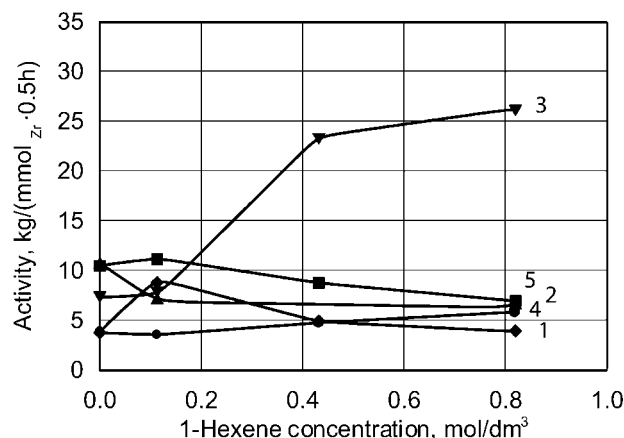
Figure 4. The effect of comonomer concentration on polymerization activity for ethylene/1-hexene copolymerization with homogeneous metallocene catalysts: (1)-(t-BuCp)$_2$ZrCl$_2$/MAO; (2)-(n-BuCp)$_2$ZrCl$_2$/MAO; (3)-(i-PrCp)$_2$ZrCl$_2$/MAO; (4)-(Me$_5$Cp)$_2$ZrCl$_2$/MAO; (5)-Ind$_2$ZrCl$_2$/MAO. The reaction conditions are the same as those given for Figure 3.

catalysts studied is shown in Table 1. We can see that titanocene gave a clearly higher grafted metal content than did the zirconocene compound having the same cyclopentadienyl ligands. These findings are contrary to those presented in literature for silica-supported Cp$_2$MCl$_2$ (M = Ti, Zr),[18] where it was observed that Ti, having a smaller atomic radius, leads to lower metal content than does zirconium (atomic radius 1.45 and 1.60 Å, respectively). When zirconocene catalysts having cyclopentadienyl and indenyl rings are compared, it is observed that the latter enables the grafting of nearly the same amount of Zr on magnesium supports. The introduction of the alkyl group into the Cp ring leads to a lower content of metallocene being immobilized in comparison with that of an unsubstituted one. However, between ligands there is no sharp difference in the final metal content. Metal loading on the magnesium support is, however, clearly lower than that obtained for a silica-supported metallocene catalyst.[18]

Catalyst Activity

The data available in the literature concerning the influence of transition metal on the activity of homogeneous and silica-supported metallocene catalytic systems clearly show the advantage of zirconium catalysts over titanium ones.[16,18,22] We decided to compare Cp$_2$MCl$_2$/MAO (M = Zr, Ti) catalysts in ethylene homo- and copolymer-

ization after their immobilization on the earlier-described magnesium carrier (Fig. 2). The zirconocene catalyst showed the highest activity.

We then undertook the investigation of the influence of the nature of ligand (Cp and Ind) and ring substituents, R, in (CpR)$_2$ZrCl$_2$ supported on a magnesium carrier on ethylene polymerization and its copolymerization with 1-hexene (Fig. 2). Comparing the nonsubstituted, three monosubstituted, and one pentasubstituted Cp catalysts, the order of their catalytic activities is (i-PrCp)$_2$ZrCl$_2$ > Cp$_2$ZrCl$_2$ > (n-BuCp)$_2$ZrCl$_2$ > (t-BuCp)$_2$ZrCl$_2$ > (Me$_5$Cp)$_2$ZrCl$_2$. The homogeneous systems, under our conditions, followed the trend n-BuCp > i-PrCp > Cp > t-BuCp = Me$_5$Cp (Fig. 3).This sequence shows us that both the electronic and steric effects are associated with R substituent influences on the activity of the catalyst. Electronic effects dominate for n-Bu and i-Pr substituents, and for the others (t-Bu and Me$_5$) the steric effect seems to be more important.

The homogeneous Ind$_2$ZrCl$_2$ catalyst is more active than that containing Cp ligands. This result is in agreement with those previously presented in literature.[3,4] The immobilization of this catalyst causes the efficiency order to be inverted. The lower activity of Ind$_2$ZrCl$_2$ might be attributed to the steric hindrance caused by the magnesium carrier surface.

Most research has shown a positive effect of higher 1-olefin introduction into polymerization

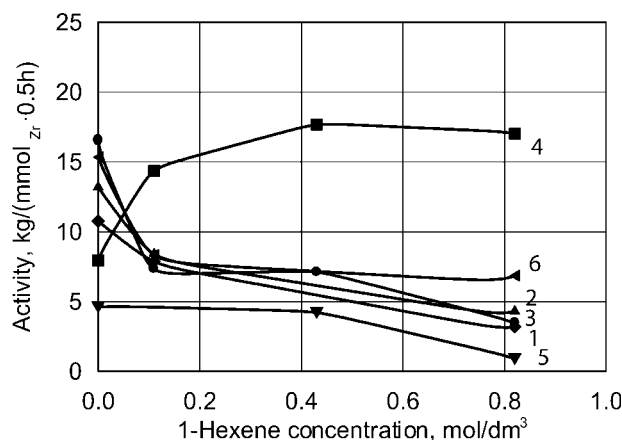**Figure 5.** The effect of comonomer concentration on polymerization activity for ethylene/1-hexene copolymerization with supported metallocene catalysts: (1)-(t-BuCp)$_2$ZrCl$_2$/MAO; (2)-(n-BuCp)$_2$ZrCl$_2$/MAO; (3)-(i-PrCp)$_2$ZrCl$_2$/MAO; (4)-(Me$_5$Cp)$_2$ZrCl$_2$/MAO; (5)-Ind$_2$ZrCl$_2$/MAO; (6)-Cp$_2$ZrCl$_2$/MAO. The reaction conditions are the same as those given for Figure 2.

Table 2. Characterization of Copolymers Obtained with Homogeneous Metallocene Systems

Catalyst	[H] (mol/dm^3)	[H] (mol %)	T_t (°C)	C (%)	M_w (10^3)	M_w/M_n
Cp$_2$TiCl$_2$[a]	–		136.1	43.0	–	–
	0.11	1.87	125.7	37.5	187.7	2.54
	0.43	4.54	133.7	–	101.6	3.07
			119.9			
Cp$_2$ZrCl$_2$	–	–	133.5	63.9	94.1	1.4
	0.11	2.59	124.8	49.1	–	–
	0.43	4.23	117.2	40.4	25.2	1.4
	0.82	6.38	110.7	39.1	6.3	3.4
(t-BuCp)$_2$ZrCl$_2$	–	–	131.5	70.0	61.0	3.77
	0.11	4.77	122.3	65.6	8.3	1.89
	0.43	8.85	111.6	46.3	5.3	1.57
	0.82	10.54	100.9	47.7	3.8	1.40
(n-BuCp)$_2$ZrCl$_2$	–	–	132.2	61.4	131.4	3.34
	0.11	2.77	124.5	50.1	45.6	5.53
	0.43	4.98	112.5	49.2	17.8	3.36
	0.82	5.22	115.1	43.1	32.3	3.50
(i-PrCp)$_2$ZrCl$_2$	–	–	132.7	62.9	116.0	4.06
	0.11	5.21	122.6	53.3	38.7	5.60
	0.43	7.46	113.0	39.7	15.5	3.07
	0.82	7.96	104.5	40.7	13.2	2.40
(Me$_5$Cp)$_2$ZrCl$_2$	–	–	133.5	77.6	48.0	3.59
	0.11	1.4	130.9	61.7	46.0	3.50
	0.43	3.2	125.6	48.8	41.0	2.40
	0.82	4.9	122.8	42.9	32.5	3.10
Ind$_2$ZrCl$_2$	–	–	134.8	58.4	121.3	3.01
	0.11	3.1	123.8	40.7	86.4	3.70
	0.43	6.1	115.4	34.2	73.6	3.35
	0.82	6.7	110.3	30.3	77.7	3.80

The reaction conditions are the same as those given for Figure 3.
[a] Reaction conditions: 0.01 mmol Ti, 14 mmol MAO; reaction time: 30 min; temperature: 25 °C.

feed on catalyst activity[23,24]; others[25–27] have shown a negative effect of increasing the concentration of comonomer on catalyst reactivity. Figures 4 and 5 indicate that the activities of both homogeneous and heterogeneous catalysts in ethylene/1-hexene copolymerization differ from those in ethylene homopolymerization. However, an enhancement of polymerization activity in the presence of a comonomer is not noted for heterogeneous catalytic systems, except for catalyst (Me$_5$Cp)$_2$ZrCl$_2$/MAO. In the case of homogeneous catalytic systems, the introduction of 1-hexene into the polymerization feed slightly increases the activity of catalysts containing Ind, t-BuCp, and Me$_5$Cp ligand; activity of (i-PrCp)$_2$ZrCl$_2$ enhances a few times, and for (n-BuCp)$_2$ZrCl$_2$ a minor decrease in activity is observed. However, with the increase in the amount of the less reactive, more sterically hindered comonomer, the majority display a drop in activity.

1-Hexene Incorporation

In any catalytic system comonomer incorporation increases with increase in initial comonomer concentration; nevertheless, the amount of comonomer incorporated mostly depends on the type of catalytic system used. Obviously, the Ziegler–Natta-type catalysts exhibit poorer efficiency than do the metallocene ones, but the efficiency of the latter is strictly connected with their structures.

To evaluate the influence of the ligand type and substituent nature as well as the transition metal in metallocene catalysts on the copolymerization performance, we studied comonomer incorporation at different comonomer/monomer feed ratios for ethylene/1-hexene copolymerization (Tables 2 and 3). Heterogenization of homogeneous metallocene systems on a magnesium carrier reduced their copolymerization ability. This effect was

observed for all catalysts, although its magnitude depended on the catalyst investigated. These results imply the high steric hindrance brought about by the presence of the support. Among the investigated supported catalysts, catalysts containing cyclopentadienyl ligands with *t*-Bu group showed the highest efficiency for incorporating 1-hexene into the polymer chain, and the one with Me_5 showed the lowest efficiency.

Comparing the catalysts with Cp and Ind ligands, the incorporation of a comonomer is similar for unsupported catalysts, and after their heterogenization a big difference in 1-hexene incorporation is observed. A greater loss of ability to incorporate 1-hexene after anchorage on the carrier surface by an Ind catalyst suggests that the presence of the bigger indenyl ligands on the support surface creates a higher steric hindrance than do cyclopentadienyl ones.

Considering the type of transition metal, Zr and Ti, the result obtained clearly shows the prevalence of the former. A supported titanium catalyst yields polymers with incorporation that is a few fold lower than that yielded by its zirconocene counterpart. In the case of homogeneous titanocene catalyst, it seems that the higher comonomer concentration in polymerization feed leads to the formation of two types of macromolecules, which clearly differ in the amount of 1-hexene incorporation (two peaks on DSC thermogram) (Fig. 6).

Molecular Weight and Other Properties

Two of the most important properties characterizing copolymers are molecular weight and molecular weight distribution. In the case of the homogeneous zirconocene catalyst, it is well

Table 3. Characterization of Copolymers Obtained with Supported Metallocene Systems

| Catalyst	[H] (mol/dm^3)	[H] (mol %)	T_t (°C)	C (%)	M_w (10^3)	M_w/M_n
Cp_2TiCl_2	–	–	142.96	36.6	473.0	3.4
	0.11	0.57	138.45	28.1	437.5	4.8
	0.43	1.42	137.67	30.4	450.3	6.4
	0.82	1.48	134.28	26.4	450.9	8.1
Cp_2ZrCl_2	–	–	136.81	50.0	119.0	2.9
	0.06	0.92	133.50	47.4	61.0	2.3
	0.11	1.49	132.09	44.8	76.0	4.9
	0.22	3.12	130.15	47.1	36.0	2.6
	0.43	5.04	126.16	44.7	21.0	2.1
	0.82	6.7	119.22	35.3	17.0	1.8
(t-BuCp)$_2$ZrCl$_2$	–	–	134.06	62.9	90.0	4.09
	0.11	3.44	123.62	57.6	24.0	2.26
	0.43	7.30	111.72	53.0	11.6	1.97
	0.82	9.29	106.29	47.2	5.0	1.50
(n-BuCp)$_2$ZrCl$_2$	–	–	134.87	46.0	218.0	1.98
	0.11	1.83	125.58	43.4	145.0	2.98
	0.43	3.08	121.71	50.7	61.5	2.86
	0.82	4.56	114.80	35.0	90.0	3.12
(i-PrCp)$_2$ZrCl$_2$	–	–	137.70	40.0	354.0	3.83
	0.11	1.48	129.98	45.5	106.8	2.10
	0.43	3.58	119.15	46.0	62.4	2.40
	0.82	4.80	116.31	47.2	37.0	2.90
(Me_5)$_2$ZrCl$_2$	–	–	138.28	46.7	199.7	2.28
	0.11	0.4	132.43	56.8	98.0	1.78
	0.43	1.1	129.6	50.6	96.6	1.89
	0.82	2.5	124.78	39.5	66.7	2.27
Ind$_2$ZrCl$_2$	–	–	136.68	56.1	–	–
	0.11	1.5	131.17	38.8	–	–
	0.43	3.1	117.32	33.4	–	–
	0.82	4.3	132.49	26.9	–	

The reaction conditions are the same as those given for Figure 2.
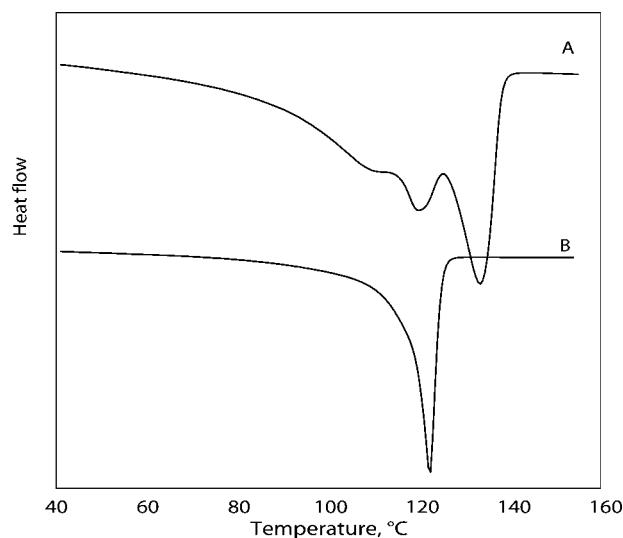
Figure 6. Comparison of the DSC curves of ethylene/1-hexene copolymers obtained over Cp_2TiCl_2/MAO (A) and $(t\text{-}BuCp)_2ZrCl_2$/MAO (B), 1-hexene incorporation 4.5 mol % for A and 4.7 mol % for B.

established that it produced polymers with low molecular weight and narrow molecular weight distribution. Homogeneous zirconocene catalysts give polyethylene with low molecular weights (from 48,000 for $(Me_5Cp)_2ZrCl_2$ catalyst to 131,400 for $(n\text{-}BuCp)_2ZrCl_2$ one; Table 2). It seems that the presence of the bulkier substituents such as t-Bu and i-Pr in Cp rings restrict, and n-Bu and five Me group simplify, the polymer chain transfer or termination. Polymers produced with a nonsubstituted Cp catalyst have lower molecular weights than those obtained with

an Ind catalyst. The average molecular weight decrease is in the following order: nBuCp > Ind > i-PrCp > Cp > t-Bu > Me_5Cp. The molecular weights of polyethylenes synthesized with a supported zirconocene catalyst are clearly higher when compared with those of the ones made with homogeneous systems, and the influence of catalyst nature on their value is retained (Fig. 7). Polyethylene synthesized with a titanocene catalyst has a molecular weight that is a few-fold higher than that synthesized with a zirconocene catalyst.

The presence of 1-hexene in polymerization feed leads to molecular weight reduction. The molecular weight of the copolymer decreases substantially when the amount of less reactive 1-hexene in polymerization feed increases (Tables 2 and 3). This effect is observed for all catalytic systems; however, it can be noted that it is connected not only with comonomer concentration in polymerization feed but also with the amount of comonomer incorporated into the polyethylene chain.

The molecular weight distribution of copolymers obtained with zirconocene catalysts mostly ranged between 1.5 and 4.0. Slightly higher values of M_w/M_n than those very often described in literature could be due to the fact that the solvent used for polymerization was hexane. Heterogenization and comonomer concentration do not have any essential influence on these values. The molecular weight distribution of polymers is, however, determined by the nature of metallocene catalyst. The lowest value of M_w/M_n is
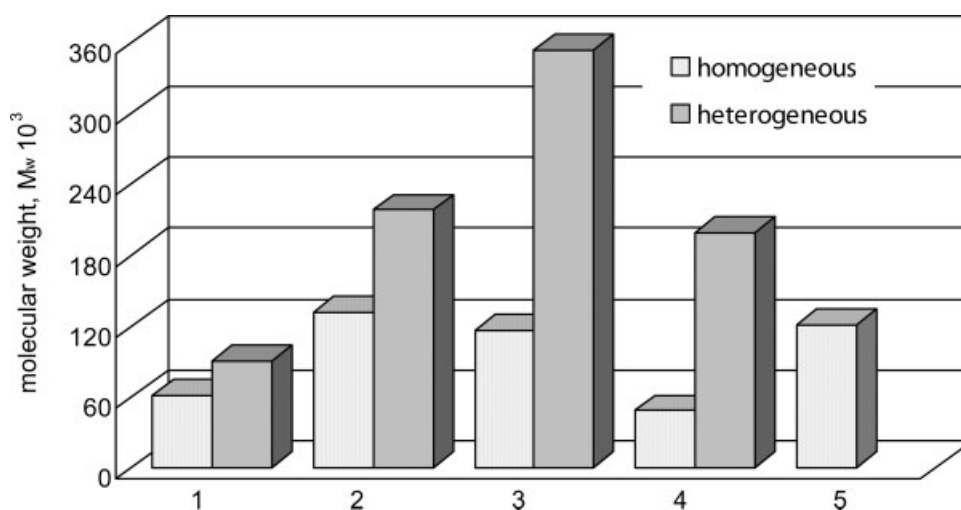

Figure 7. Comparison of molecular weight of PE obtained with homogeneous and supported zirconocene catalysts: (1)-$(t\text{-}BuCp)_2ZrCl_2$/MAO; (2)-$(n\text{-}BuCp)_2ZrCl_2$/MAO; (3)-$(i\text{-}PrCp)_2ZrCl_2$/MAO; (4)-$(Me_5Cp)_2ZrCl_2$/MAO; (5)-Ind_2ZrCl_2/MAO.

shown by polymers obtained with Cp and *t*-BuCp catalysts. A titanocene catalyst, especially after heterogenization, gives a polymer with much more differential macromolecules.

Tables 2 and 3 also include data on other polymer properties. As can be seen, the crystallinity of polyethylene made with homogeneous zirconocene catalysts ranged from 60 to 80%. The supporting of these catalysts caused a decrease in the crystallinity of the synthesized polyethylenes, on an average by dozen percent. Heterogenization also leads to an increase in the melting point of the obtained polymers by about 2–4°. Melting temperatures and crystallinities change with polymer composition and the extent of 1-hexene incorporations. The highest degree of incorporated comonomer leads to the lowest melting temperature and crystallinity, as expected.

CONCLUSIONS

The ligand structure, transition metal type, and heterogenization have been demonstrated to have significant influence on the polymerization and copolymerization behavior of metallocene catalysts. Zirconocene catalysts have a privilege over titanocene ones in the activity and efficiency of the comonomer incorporated. The latter, however, produce polymers with higher molecular weight, which improves their processing.

Among the investigated zirconocene catalysts, $(t\text{-BuCp})_2\text{ZrCl}_2$ exhibits the highest ability to incorporate a comonomer, more than 10 mol% at 0.82 mol/dm^3 concentration in the feed, and this ability is only slightly reduced after its heterogenization. This reduction in comonomer incorporation after catalyst supporting is similar to those obtained with other catalytic systems that have been investigated. The supporting of a metalocene catalyst on the carrier also brings about positive changes, such as an increase in molecular weight and melting temperature of the polymers.

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