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Magnesium chloride modified with organoaluminium compounds as a support of the zirconocene catalyst for ethylene polymerisation

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Abstract

This work describes the influence of the modification of the $MgCl_2(THF)_2$ and $MgCl_2$ magnesium supports with the $AlEt_2Cl$, MAO, $AlEt_3$, $AlMe_3$, and $AlEt_2Cl$ alkylaluminium compounds on heterogenisation of the bis(cyclopentadienyl) zirconium(IV) dichloride Cp_2ZrCl_2 catalyst. It was found that only the $MgCl_2(THF)_2$ support modified with $AlEt_2Cl$ gave the heterogeneous catalyst. On the contrary, application of a magnesium carrier modified by $AlEt_3$, $AlMe_3$, and MAO compounds only results in a homogeneous zirconocene catalyst.

Keywords: Metallocene catalysts; Polyethylene (PE); Magnesium dichloride support; Molecular weight distribution

1. Introduction

The discovery of metallocene catalysts, which when used with a methylaluminoxane (MAO) cocatalyst were revealed to be highly active for homogeneous polymerisation of α-olefins [1–6], aroused an economic interest, as it became clear that they could compete with Ziegler–Natta catalysts. These new generation catalysts are capable of producing a variety of polyethylene copolymers, all with different chain compositions and architecture, and polypropylene with tailored microtacticities. However, they are more active than Ziegler–Natta catalysts only as homogeneous metallocene systems. To use metallocene catalysts in modern gas-phase olefin polymerisation processes, they need to be heterogenised on a support. Unfortunately, activities of supported systems are generally reduced with respect to those of homogeneous systems [7–9]. Therefore, the development of metallocene catalysts, which are supported on a solid carrier surface, and have activities comparable to homogeneous ones, has been a point of major interest in recent years [10–16].

The most widely used supports for metallocene catalysts are inorganic solids such as SiO_2, Al_2O_3, zeolite, and $MgCl_2$. The scarce literature data available concern the use of $MgCl_2$ as a support for metallocene catalysts. This lack of interest cannot be justified as the $MgCl_2$, modified by an electron donors compound, is the most commonly used support of modern Ziegler–Natta catalysts.

Table 1 presents the literature reports concerning the metallocene catalysts supported on $MgCl_2$ and applied for the ethylene polymerisation. The homogeneous zirconocene catalysts found in these publications are also presented for comparison. As can be seen, the polymerisation reactions were slurry experiments mostly carried out in the aromatic solvent; toluene or xylene, as is appropriate for homogenous catalysts, rather than in the aliphatic solvent; hexane or heptane. The majority of

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Table 1
Magnesium chloride supported metallocene catalysts for ethylene polymerisation; their selected properties, the properties of the PE produced, and polymerization conditions[a]

Catalyst	Support	Modifier	Activity (kg PE/g Mt·h)	Al/Mt (mol/mol)	$M_w \cdot 10^{-3}$ (g/mol)	MWD	T (°C)	p (MPa)	Solvent	Ref.
Cp_2ZrCl_2	–	–	45	5000	–	–	70	0.10	Heptane	[17]
Cp_2ZrCl_2	$MgCl_2(THF)_2$	TIBA	9	5000	43	1.85	70	0.10	Xylene	[17]
Cp_2ZrCl_2	$MgCl_2(THF)_2$	TMA	88	5000	63	2.10	70	0.10	Xylene	[17]
Cp_2ZrCl_2	$MgCl_2(THF)_2$	Not present	59	5000	61	2.48	70	0.10	Xylene	[17]
Cp_2ZrCl_2	$MgCl_2(THF)_2$	Not present	38	5000	39	2.15	70	0.10	Heptane	[17]
Cp_2ZrCl_2	$MgCl_2(THF)_2$	Not present	54	8000	130	2.2	50	0.50	Hexane	[18]
$CpZrCl_3$	$MgCl_2$/2-ethylhexanol/ $Ti(OEt)_4$	DEAC	274	21,000	450	8.0	70	0.60	Hexane	[19]
Cp_2ZrCl_2	–	–	17	1000	–	3.4	50	0.13	Toluene	[20]
Cp_2ZrCl_2	$SiO_2/MgCl_2$	MAO	8	1000	–	3.2	50	0.13	Toluene	[20]
Cp_2ZrCl_2	$SiO_2/MgCl_2$	TMA	11	1000	–	2.7	50	0.13	Toluene	[20]
Cp_2ZrCl_2	$MgCl_2 \cdot 4CH_3OH$	TIBA	28	3000	66	3.4	70	0.13	Toluene	[21]
Cp_2ZrCl_2	$MgCl_2$/EB	Not present	11	2000	159	2.0	60	0.11	Toluene	[22]
Cp_2ZrCl_2	$MgCl_2$/EB	MAO	16	2000	179	2.0	60	0.11	Toluene	[22]
$Et(Flu)_2ZrCl_2$	$MgCl_2$/EB	MAO	0.4	2000	691	2.2	60	0.11	Toluene	[22]
$Me_2Si(Ind)_2ZrCl_2$	–	–	1470	26,000	–	–	80	0.60	Toluene	[23]
$Me_2Si(ind)_2ZrCl_2$	$MgCl_2$	TEA + CCl_4	73	1500[b]	–	–	80	0.60	Hexane	[23]
$Me_2Si(Ind)_2ZrCl_2$	$MgCl_2$	TEA + CCl_4	31	2000	–	–	80	0.60	Toluene	[23]
Cp_2ZrCl_2	–	–	86	37,000	106	2.14	50	0.15	Toluene	[24]
Cp_2ZrCl_2	$MgCl_2 \cdot 4CH_3OH$	TIBA	22	15,000	440	3.5	50	0.15	Toluene	[24]
rac-$Et[Ind]_2ZrCl_2$	$MgCl_2 \cdot 3.33C_2H_5OH$	TIBA	8	15,000	360	3.7	50	0.15	Toluene	[24]

[a] Cocatalyst MAO.

[b] Cocatalyst TIBA.

the $MgCl_2$ supports are complexes with donor compounds such as tetrahydrofuran (THF), ethyl benzoate (EB), MeOH, and EtOH. Modification of these complexes with alkylaluminium compounds ($Al(i\text{-}Bu)_3$, $AlMe_3$, and MAO) increases the activities of the supported catalysts [17,18,20–24] up to the value 88 kg PE/g Zr · h. In one study [19], the mixture of Cp_2ZrCl_2 and $Ti(OEt)_4$ was used as a catalyst supported on $MgCl_2$ modified by $AlEt_2Cl$. This led to higher activity (274 kg PE/g Zr · h) and the PE obtained had a molecular weight of 450,000 g/mol and a relatively broad molecular weight distribution (MWD) of the value 8. A similar influence of $Ti(OR)_4$ compounds on the properties of PE was observed in the case of the Ziegler–Natta catalyst [25].

Considering the literature data listed in Table 1 and our previous investigations [18], in the presented work the Cp_2ZrCl_2 metallocene catalyst was subjected to heterogenisation on the $MgCl_2(THF)_2$ complex modified with $AlEt_2Cl$ and MAO and applied for the polymerisation of ethylene. Additionally, the anhydrous commercial magnesium chloride, modified with $AlEt_3$ and $AlMe_3$ was used as a support without an internal Lewis base. To simplify the method for metallocene supporting, the successive washing and drying steps were omitted, which may be more attractive from a commercial point of view. Also, such a prepared catalyst in some way mimics metallocene supported in situ [26–28].

2. Experimental part

2.1. Materials

Ethylene (Petrochemia SA, Pock) and pure nitrogen (Polgaz) were used after having been passed through a column of sodium metal supported on Al_2O_3. Pure-grade hexane (Petrochemia SA, Pock) was refined with sulfuric acid, dried by refluxing in nitrogen over sodium metal, and stored over 4A molecular sieves. Toluene (POCh, Gliwice) was distilled over sodium metal and stored over 4A molecular sieves. Bis(cyclopentadienyl)zirconium dichloride—Cp_2ZrCl_2 (Fluka), methylaluminoxane—MAO (10 wt.% as toluene solution, Witco), $AlEt_2Cl$—diethylaluminium chloride (Schering) were applied without additional purification. Tetrahydrofuran (Fluka) was purified according to the standard method using NaOH, metallic Na and benzophenone as an indicator. Anhydrous magnesium chloride (98 wt.%) (Fluka) dried for 2 h at 393 K.

2.2. $MgCl_2(THF)_2$ complex support

Anhydrous magnesium chloride was mixed with tetrahydrofuran for 24 h at room temperature by using $THF/MgCl_2$ molar ratio = 20. The $MgCl_2(THF)_2$ complex was precipitated by means of purified *n*-hexane, then filtered off, washed thoroughly with *n*-hexane and dried. The support obtained contained 9.39 wt.% Mg as determined by the atomic absorption spectrometry (AAS) method, which is in agreement with the molecular formula $MgCl_2(THF)_2$. The complex character of the $MgCl_2(THF)_2$ support was determined by FTIR analysis, which reveals a band of tetrahydrofuran bounded to magnesium chloride at 1033 cm^{-1}, whereas a band of free THF at 1080 cm^{-1} is not present.

2.3. Catalysts preparation

Two catalysts were obtained by using $MgCl_2(THF)_2$ as a support, modified with $AlEt_2Cl$ (catalyst **A**) or MAO (catalyst **B**). The support was prepared by milling $MgCl_2(THF)_2$ with $AlEt_2Cl$ or MAO in a glass mill (capacity: 250 cm^3, with 20 balls of 0.5–0.7 cm diameter) in a toluene solution at room temperature for 1 h using an equimolar ratio of substrates. The zirconium catalyst was prepared by milling the obtained suspension of the modified support with a toluene solution of Cp_2ZrCl_2 using the Mg/Zr molar ratio = 10, at room temperature for 24 h.

Two other catalysts were obtained by using $MgCl_2$ as a support modified with $AlEt_3$ (catalyst **C**) or $AlMe_3$ (catalyst **D**). A solution of AlR_3 in toluene (10–14 wt.%) was added dropwise for 1 h at 273 K to a vigorously stirred suspension of magnesium chloride in toluene (6.3 wt.%) to achieve the Al/Mg molar ratio = 4 in the mixture. Then the mixture was heated for 5 h at 331–333 K. Each operation was carried out in a nitrogen atmosphere. The zirconium catalyst was prepared by milling the obtained suspension of the modified support with a toluene solution of Cp_2ZrCl_2 using the Mg/Zr molar ratio = 10, at room temperature for 24 h.

All steps were carried out in oxygen-free conditions using an inert nitrogen atmosphere. The obtained suspensions of the catalysts **A**–**D** were applied to ethylene polymerisation.

2.4. Polymerisation procedure

Ethylene polymerisation was conducted under nitrogen atmosphere in a 1-dm^3 stainless steel autoclave equipped with a stirrer and a heating jacket. First, measured amounts of hexane (700 cm^3), MAO, and the catalyst suspension were added successively into the reactor ($Al_{MAO}/Zr = 4000$). Subsequently, ethylene was introduced and subjected to polymerisation at constant temperature and under constant ethylene pressure ($T = 50$ °C, $p = 0.5$ MPa). The reaction was terminated by releasing the pressure in the reactor and by adding methanol to deactivate the catalyst. The product was poured into a dilute solution of hydrochloric acid in methanol. The polymer obtained was filtered off, washed with methanol, and dried.

2.5. Polymers characterisation

In our work we found that methylaluminoxane decomposition products contaminate the polymer obtained and only HF dissolves these products. Therefore, the samples of PE were purified before their molecular masses were determined. The samples were washed with 5% HCl in methanol, 10% HF in methanol, pure methanol, and filtered off and dried after each step [29].

Molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC, Waters 150-CV) using 1,2,4-trichlorobenzene as a solvent at 142 °C. The data were analysed using polystyrene calibration curves.

Particle size analysis of the PE was performed by means of sieve method using a vibrating screen (Frisch Company). Constant weight samples were shaken for 20 min, using a set of sieves with the sieve mesh 0.09–2.0 mm. The weight of each fraction was recorded and the weight percentage calculated. The average particle diameter $a_{1,2}$ was calculated as $a_{1,2} = (a_1 \cdot a_2)^{0.5}$ where a_1 and a_2 are the mesh diameters of the top and bottom sieves, respectively.

The FT-IR analysis was performed using a Philips Analytical PU 9800 spectrometer, resolution $R = 2$ cm^{-1}, bands 4000–400 cm^{-1}, in Nujol KBr/KBr.

The amount of magnesium in the support was determined by the AAS method, using the SOLAR 969 Unicam spectrometer.

3. Results and discussion

Table 2 presents the activities of the studied catalyst systems **A**–**D** and selected properties of the polyethylene obtained in similar reaction conditions. It should be noticed that the studied catalysts, when using the magnesium chloride as a carrier modified with the alkylaluminium compounds, are more active than those presented in Table 1 [17,18,20–24]. On the other hand, however, the properties of the PE produced, i.e. the molecular weight and bulk density, are not satisfactory.

Analysis of the kinetic curves reveals that the studied catalysts **A**, **C**, and **D** do not show polymerisation-rate decay as a function of time (Fig. 1), which is an attractive feature of the heterogeneous systems as compared to the homogeneous ones [26,29–32]. The proportional increase of the PE yield with time for the catalysts **C** and **D** with $MgCl_2$ modified with $AlEt_3$ or $AlMe_3$, shows that the ethylene polymerisation reaction rates are constant. For catalyst **B**, the proportional increase of the PE yield with time can be seen only up to 45 min. In the case of catalyst **A**, which is supported on $MgCl_2(THF)_2$ modified with $AlEt_2Cl$, the proportional increase of the PE yield appears after about 45 min of the polymerisation reaction.

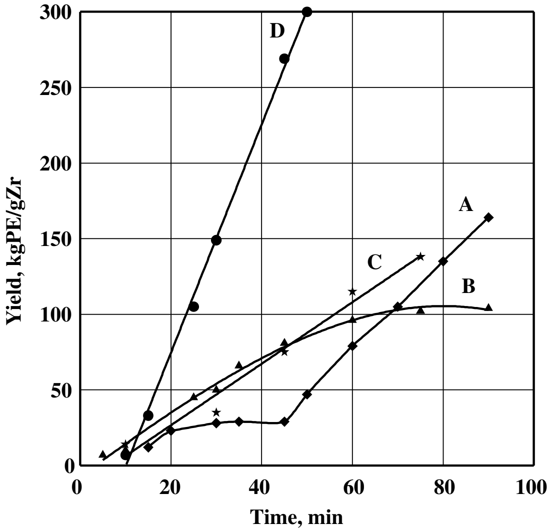

Fig. 1. Influence of the polymerisation time on the yield of the PE produced with catalysts **A**–**D** (see Table 2). Polymerisation conditions: **A**, **B** [Zr] = 5×10^{-6} mol/dm^3, Al/Zr = 4000; **C** [Zr] = 2×10^{-6} mol/dm^3, Al/Zr = 6000; **D** [Zr] = 2×10^{-6} mol/dm^3, Al/Zr = 10,000.

Table 2
Activities of the studied catalyst systems activated with MAO and selected properties of the PE produced[a]

Catalyst	Activity (kg PE/g Zr h)	$M_w \times 10^{-3}$ (g/mol)	MWD	Bulk density (g/dm^3)
(A) $MgCl_2(THF)_2/AlEt_2Cl/Cp_2ZrCl_2$	94.2	148.9	3.2	72
(B) $MgCl_2(THF)_2/MAO/Cp_2ZrCl_2$	101.0	135.6	2.8	62
(C) $MgCl_2/AlEt_3/Cp_2ZrCl_2$	75.3	72.4	2.0	59
(D) $MgCl_2/AlMe_3/Cp_2ZrCl_2$	134.9	97.9	1.8	53
$MgCl_2(THF)_2/Cp_2ZrCl_2$[b]	54.8	130.5	2.2	45

[a] Polymerisation conditions: [Zr] = 5×10^{-6} mol/dm^3, Al/Zr molar ratio = 4000.
[b] Al/Zr molar ratio = 8000 [18].

The analysis of the morphology of the PEs obtained over catalysts **B** (Fig. 2) and **D** (Fig. 3) shows that their particle size distributions are monomodal. However, in the case of catalyst **A**, the particle size distribution of the PE obtained in the first 30 min of the polymerisation reaction is monomodal, whereas those obtained after 60 and 90 min are bimodal (Fig. 4).

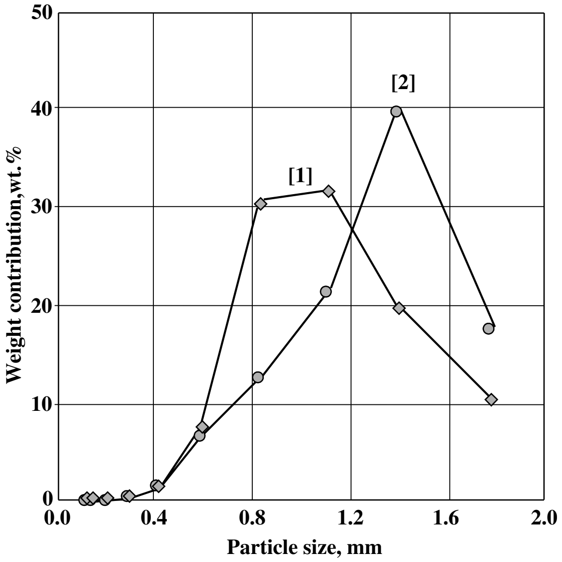

Fig. 2. Particle size distribution of the PE obtained with catalyst **B** [$MgCl_2(THF)_2/MAO/Cp_2ZrCl_2 + MAO$] during polymerisation time: curve [1] = 35 min, curve [2] = 60 min. Polymerisation conditions: $[Zr] = 5 \times 10^{-6}$ mol/dm^3, $Al_{MAO}/Zr = 4000$.

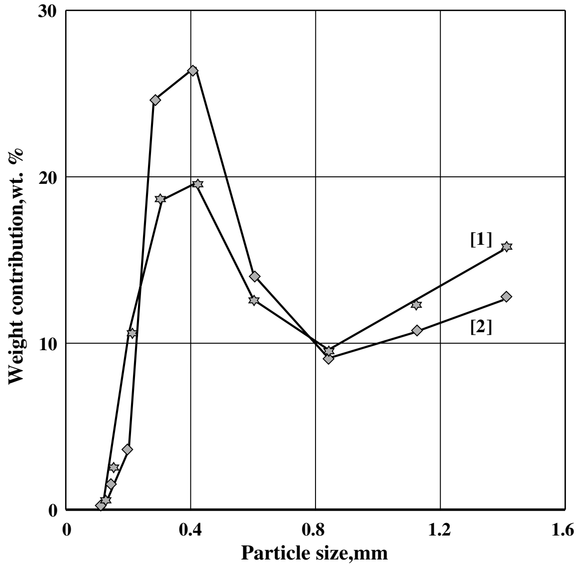

Fig. 3. Particle size distribution of the PE obtained with catalyst **D** [$MgCl_2(THF)_2/AlMe_3/Cp_2ZrCl_2$ + MAO] during polymerisation time: curve [1] = 45 min, curve [2] = 75 min. Polymerisation conditions: $[Zr] = 2 \times 10^{-6}$ mol/dm^3, $Al_{MAO}/Zr = 10{,}000$.

Therefore, the shape of the molecular weight distribution curves were analysed, as in the case of [21,27,33–35]. As seen in Fig. 5, the shapes of the MWD curves of the PEs produced on catalysts **C** and **D** are monomodal, which means that only one kind of active site is present in these catalysts. In the case of catalyst **B**, the MWD

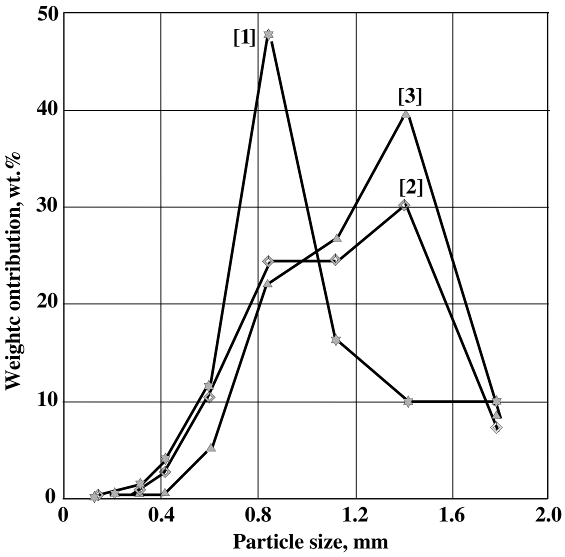

Fig. 4. Particle size distribution of the PE obtained with catalyst **A** [$MgCl_2(THF)_2/AlEt_2Cl/Cp_2ZrCl_2 + MAO$] during polymerisation time: curve [1] = 30 min, curve [2] = 60 min, curve [3] = 90 min. Polymerisation conditions: $[Zr] = 5 \times 10^{-6}$ mol/dm^3, $Al_{MAO}/Zr = 4000$.

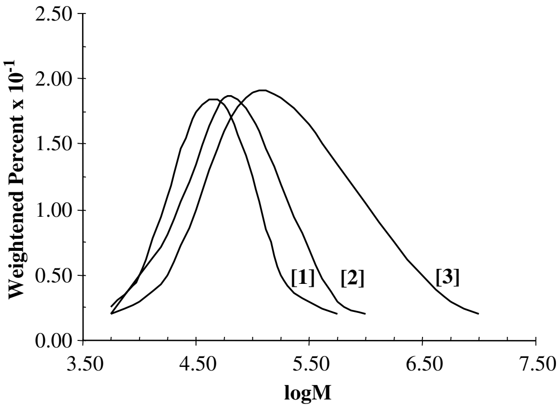

Fig. 5. Molecular weight distributions of the PE obtained after 90 min of the polymerisation reaction using catalyst: **D**—curve [1], **C**—curve [2], **B**—curve [3].

curve also show monomodal character although broader (2.8). However, the shape of the MWD curve of PE produced by catalyst **A** is quite different (Fig. 6). After 30 min of the polymerisation reaction, MWD is monomodal (curve 1), whereas after 60 and 90 min it changes to bimodal (curves 2 and 3).

The dependence of the molecular weights of the PEs produced over catalysts **A**, **B**, and **D** on the polymerisation reaction time, also shows a different character of catalyst **A** (Fig. 7). For catalyst **B** (curve 1), the molecular weights of the PEs increase with the polymerisation time and for catalyst **D** (curve 2) it is nearly constant. For catalyst **A**, an increase and thereafter a decrease of molecular weight of polyethylene is observed (curve 3).

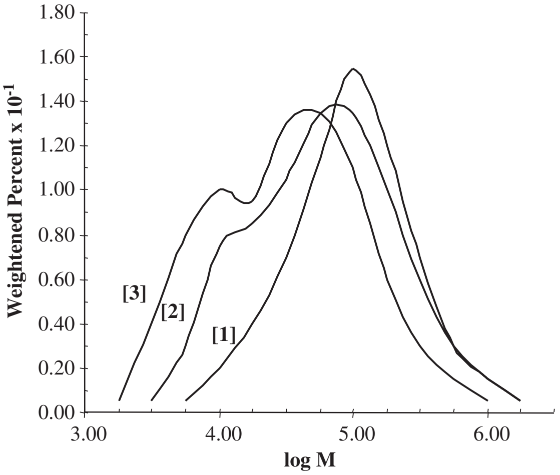

Fig. 6. Molecular weight distributions of the PE obtained using catalyst **A** [$MgCl_2(THF)_2/AlEt_2Cl/Cp_2ZrCl_2$ + MAO]: curve [1] = 30 min, curve [2] = 60 min, curve [3] = 90 min.

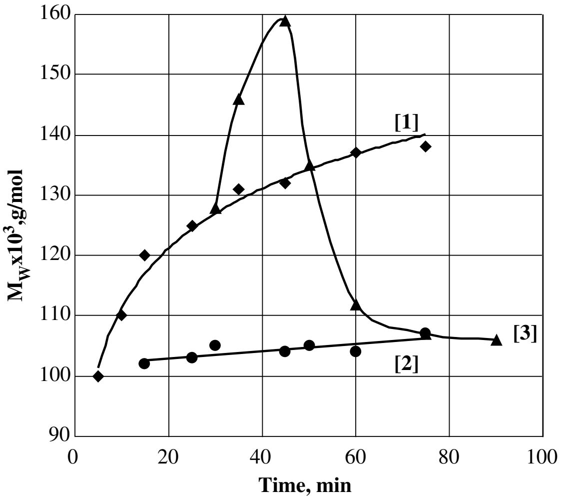

Fig. 7. Molecular weight of the PE obtained as a function of the polymerisation time for catalyst: **B**—curve [1], **D**—curve [2], **A**—curve [3].

The kinetic results of catalyst **A** (Fig. 1) as well as the morphology (Fig. 4), MWD (Fig. 6) and M_w (Fig. 7) of the PE obtained show that this catalyst is different from catalysts **B**, **C** and **D**. Certainly, more than one kind of active site is present on catalyst **A**. One appears at the beginning of the polymerisation reaction, and another, after about 45 min (Fig. 1, curve A). The higher value of the molecular weight of PE produced during the first 45 min of the polymerisation (Fig. 7, curve 3) means that chain growth takes place on heterogeneous active sites. The following decrease of the PE molecular weight means that, after 45 min, the polymerisation reaction takes place on another kind of active site—probably homogeneous.

The relatively high activities of the studied catalysts **A**–**D** in the ethylene polymerisation (Table 2) as compared to the literature data (Table 1), as well as a lack of the polymerisation-rate decay as a function of time (Fig. 1) suggest their heterogeneity. On the other hand, the properties of the PE, i.e. the low molecular weight ($M_w \leqslant 150{,}000$ g/mol), and the very low bulk density, ($d_N \leqslant 80$ g/dm^3), are similar to those of the PEs produced over the homogeneous catalysts [26,36,37].

These results, together with the data concerning catalyst **A** do not show whether the catalysts are heterogeneous or homogeneous. Therefore, in further investigations the ethylene polymerisation was performed with catalysts **A**, **B** and **C** not in the form of suspension, but as solids—after the filtering, washing and drying steps. For comparison, the obtained filtrates were also applied in the ethylene polymerisation. The results are presented in Table 3.

As can be seen, the filtrates of catalyst **B** and **C** show catalytic activities equal to the suspensions, whereas their solids do not reveal any activities. It means that the modification of the magnesium chloride supports with $AlEt_3$, $AlMe_3$ or MAO does not result in heterogenisation of the Cp_2ZrCl_2 compound. In the case of catalyst **A**, the filtrate also shows some catalytic activity but smaller than when in suspension. However, in contrary to catalysts **B** and **C**, its solid does reveal some catalytic activity. This means that partial heterogenisation takes place. Therefore, the catalyst system **A**, in which the support was modified with $AlEt_2Cl$, contains both homogeneous and heterogeneous active sites. On the basis of the results obtained, it can be assumed that by changing the method of preparation of catalyst **A** (including the washing and drying steps of the catalyst in each stage of its synthesis) the heterogeneous zirconocene catalyst can be obtained. $AlEt_2Cl$ seems to be the modifier which enables the efficient anchorage of the zirconocene compound to the $MgCl_2(THF)_2$ support.

Table 3
Polymerisation yields and bulk densities of the PE produced for the investigated catalysts **A**–**C**

Catalyst	Suspension		Filtrate		Solid	
	Yield	Bulk density	Yield	Bulk density	Yield	Bulk density
(A) $MgCl_2(THF)_2/AlEt_2Cl/Cp_2ZrCl_2$	35.8	72	26.8	60	7.65	112
(B) $MgCl_2(THF)_2/MAO/Cp_2ZrCl_2$	46.0	62	47.4	56	–	
(C) $MgCl_2/AlEt_3/Cp_2ZrCl_2^a$	22.4	58	22.1	33	–	

Polymerisation conditions: medium-hexane (700 ml), $T = 50$ °C, $p = 0.5$ MPa, $t = 60$ min, catalyst **A**, **B** $[Zr] = 5 \times 10^{-6}$ mol/dm^3, Al/Zr molar ratio = 4000, catalyst **C** $[Zr] = 2 \times 10^{-6}$ mol/dm^3, Al/Zr molar ratio = 6000.
Yield: g PE/hexane volume, Bulk density: g/dm^3.

4. Conclusion

$MgCl_2(THF)_2$ and $MgCl_2$ magnesium supports were modified with the alkylaluminium compounds ($AlEt_2Cl$, MAO and $AlMe_3$, $AlEt_3$, respectively) and applied to heterogenisation of the Cp_2ZrCl_2 zirconocene catalyst, which after activation by MAO, was investigated in the ethylene polymerisation. The effect of the reaction time on the yield of the ethylene polymerisation was studied. The properties of the polyethylenes produced i.e. molecular weight, molecular weight distribution, bulk density, and particle size distribution were determined.

The studied catalyst systems reveal good activity as compared to the magnesium chloride supported catalyst known from literature data. They did not show polymerisation-rate decay as a function of time, in contrast to homogeneous catalysts.

The obtained results lead to the interesting conclusion that the immobilisation of the zirconocene catalyst on the $MgCl_2$ and $MgCl_2(THF)_2$ supports modified with $AlMe_3$, $AlEt_3$ and with MAO, respectively, does not result in obtaining a heterogeneous catalyst. On the contrary, the modification of the $MgCl_2(THF)_2$ complex with $AlEt_2Cl$, the alkylaluminium compound containing chlorine atom, lead to the heterogeneous catalyst. This heterogeneous zirconocene catalyst supported on the $MgCl_2(THF)_2$ complex modified with $AlEt_2Cl$ is under investigation.

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