

# Ethylene polymerisation with hafnocene difenolate/MAO system: a comparison with other hafnocenes

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## Abstract

NMR spectra of new catalyst  $\text{Cp}_2\text{Hf}(\text{OFI})_2$  (where  $\text{OFI} = -\text{OC}_{10}\text{H}_{17}$  is a deprotonated moiety of fenchyl alcohol, endo-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol) and its catalytic behaviour in homogeneous ethylene polymerisation activated by MAO are discussed in comparison with known  $(\text{Cp}_2\text{HfCl}_2/\text{MAO})$  and previously studied  $(\text{Cp}_2\text{Hf}(\text{OMAd})_2/\text{MAO})$ , where  $-\text{OMAd}$  is a deprotonated moiety of 2-methyl-2adamantanol systems. The influence of  $\sigma$ -bonded bridged alicyclic alcoholato-ligand on polymerisation process and final polymer properties is shown. The dependencies of the catalytic activity of these systems and those of  $M_w$  of the polyethylene obtained versus independent and dependent variables of the polymerisation process are compared and discussed.

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**Keywords:** Metallocenes; Catalytic behaviour; NMR spectra; Alicyclic alcoholato-ligand

## 1. Introduction

Homogeneous catalytic systems based on transition metal metallocenes have been a focus of intense investigation for more than two last decades, since Kaminsky and Sinn succeed to polymerise olefins using methylaluminumoxane (MAO) activator [1,2]. Such systems are often more active with respect to conventional heterogeneous Ziegler–Natta catalysts and have a single species of the active centre. Hence, homogeneous catalysts offer a possibility of fine tuning and better control over the polymer microstructure and properties. The research activities have mainly been concentrated on the influence of different  $\eta^5$ -bonded aromatic ligands on the transition metal active site [3,4], as far as their effect is dominant. The in-

fluence of  $\sigma$ -bonded ligands on monomer co-ordination, the rate of chain propagation and chain termination reactions was underestimated, inter alia due to their small dimensions with respect to the rest of the complex. However, a substitution at the coordination centre of  $\sigma$ -bonded chloro-ligands for other groups represents an interesting approach that is capable to change a performance of the catalyst, as well as to give polymers with new microstructures [5–10]. The substitution to  $-\text{CH}_3$  changes the polymerisation rate [5], the substitution by  $-\text{F}$  or alcoholato-moieties improves the catalytic activity, moreover, for the system  $\text{CpTiCl}_2(\text{OR})/\text{MAO}$  ( $\text{R} = \text{Me}, \text{Et}, \text{iPr}$ ) a syndiospecificity is also increased [6,7,10]. Finally, a binaphtholate of zirconocene produces a considerable fraction of non-cycled units in 1,5-hexadiene cyclopolymerisation [8,9].

From this point of view, group 4 metallocene complexes with sterically hindered  $\sigma$ -bonded ligands represent a particular interest. During the last decade we studied the effect of these ligands on a catalytic performance of group 4

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metallocene coordination compounds in the homogeneous olefin polymerisation activated by MAO, as well as their influence on the final polymer properties [11–14]. This research is providing a necessary knowledge about a specific role of each several component of the metallocene/MAO catalytic system in order to enable a creation of its integral model. Independently, the necessity for a systematic study of the role of  $\sigma$ -ligands was also expressed by Zanella and coworkers [15], and Niu and Hall [16].

In the present work, we discuss the relevance of the  $\sigma$ -bonded bridged alicyclic alcoholato-ligands in ethylene polymerisation catalysed by hafnocene/MAO system.

## 2. Experimental

All reactions were carried out under purified nitrogen atmosphere using glove-box and Schlenk techniques.

### 2.1. Materials

Research grade ethylene and nitrogen gases were purified by passing through columns with molecular sieves 3 Å and Cu catalyst. MAO was donated by Crompton GmbH as 10 wt.% solution in toluene and was used as received. Toluene was purified by reflux and distillation over Na/benzophenone. The difenolate of hafnocene was synthesised as described in [17].

### 2.2. Ethylene polymerisation

The polymerisation was performed in a 500 ml autoclave equipped with mechanical stirrer. Hundred millilitres of toluene and a half amount of MAO were added to the reactor under nitrogen atmosphere. Subsequently, the reactor was saturated with ethylene at 200 kPa and the experimental temperature. Separately, the metallocene catalyst was brought in contact with the rest of MAO in a Schlenk flask. After 10 min of contact, this solution was injected into the reactor. The reaction was carried out for 1 h. Polymerisation rate was determined from the consumption rate of the monomer, measured by a hot-wire flowmeter (model 5850D, Brooks Instruments) connected to a PC through an A/D converter. The polymerisation was terminated by addition of ethanol acidified by HCl. The polymer was washed up with plenty of ethanol and vacuum dried at 60 °C.

The reactions with hydrogen were carried out according to the same procedure. The required quantity of hydrogen was introduced before the monomer.

The polymerisation was performed in 5 l a steel autoclave equipped with a temperature regulator and rake stirrer. Two litres of hexane freshly distilled over K/benzophenone were introduced into the reactor under N<sub>2</sub> atmosphere. The reactor was saturated with ethylene at 1450 kPa, and 50 kPa of H<sub>2</sub> was added. Subsequently, a freshly prepared toluene solution containing 10  $\mu$ mol of the hafnocene complex and 27 mmol

of MAO was injected. The reaction was carried out for 1 h. The polymer was washed up with plenty of ethanol and vacuum dried at 60 °C.

### 2.3. NMR spectra

All spectra were recorded on Bruker AC-200 NMR-spectrometer at 293 K in C<sub>6</sub>D<sub>6</sub> versus TMS as internal standard. The samples were prepared in a dry-box, the <sup>1</sup>H and <sup>13</sup>C spectra were recorded at 200.13 and 50.33 MHz, respectively.

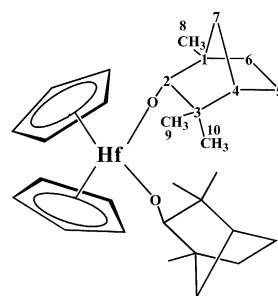
### 2.4. Polymer characterisation

The melting temperature ( $T_m$ ) and the crystallinity degree ( $x_c$ ) of the polymers were determined by differential scanning calorimetry (DSC) technique in the temperature range of 50–250 °C and the heating rate of 10 °C/min. The  $x_c$  was calculated using  $\Delta H_{0\text{ethylene}} = 292 \text{ J/mol}$  value.

The weight-average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) of the polymers were determined by gel permeation chromatography (GPC) on Waters 150CV plus instrument at 135 °C using a set of  $\mu$ Styragel HT6E, HT3, HT4 columns (Waters), monodisperse polystyrene calibration standard, and trichlorobenzene solvent.

## 3. Results and discussion

Group 4 metallocene complexes with  $\sigma$ -bonded bridged alicyclic ligands represent a particular interest due to a great volume of such ligands, comparable with that of the coordination centre. According to our estimate of a steric shielding potential of the ligand, a deprotonated moiety of 1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol (fenchyl alcohol) has a maximum shielding capacity among a series of bridged bi- and tricyclic alcohols [18]. We synthesised a coordination compound of hafnocene with fencholato-ligand in order to investigate the influence of the steric hindrance of this  $\sigma$ -ligand on the performance of hafnocene/MAO catalytic system and properties of the resulting polymers.



As one may observe from the structural formula of fenchyl alcohol, an introduction of four substituents into the symmetric bicyclo[2.2.1]heptane moiety results in a loss of symmetry. Each position in the molecule becomes non-equivalent, hence protons of the bicyclic moiety give rise to rather complex and overlapping multiplet signals. Assignment for both

Table 1  
 $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of fenchyl alcohol and difenholate of hafnocene

$^{13}\text{C}$ NMR				$^1\text{H}$ NMR			
Position	FIOH	$\text{Cp}_2\text{Hf}(\text{OFI})_2$	$\Delta^a$	Position	FIOH	$\text{Cp}_2\text{Hf}(\text{OFI})_2$	$\Delta^a$
C1	49.38	51.22	1.84	H2	3.16	3.62	0.46
C2	84.90	97.76	12.86	H4	1.57	1.60	0.03
C3	39.37	41.52	2.15	H5endo	1.63	1.69	0.06
C4	48.37	48.43	0.06	H5exo	1.35	1.40	0.05
C5	26.52	26.85	0.33	H6endo	1.78	1.74	-0.04
C6	25.48	26.08	0.60	H6exo	0.92	- <sup>b</sup>	-
C7	41.31	41.09	-0.22	H7anti	0.99	1.03	0.04
C8	19.84	20.42	0.58	H7syn	1.30	1.35	0.05
C9	30.93	31.11	0.18	8	1.07	1.11	0.04
C10	20.70	21.95	1.25	9	0.91	0.99	0.08
$\text{Cp}^c$		112.12	-2.26	10	0.85	0.87	0.02
				$\text{Cp}^c$	-	5.92	0.11
				OH	2.41	-	-

<sup>a</sup> Positive  $\Delta$  value corresponds to downfield shift of the signal, and negative value corresponds to the upfield one.

<sup>b</sup> Not registered due to overlap with intense signal of the methyl group.

<sup>c</sup> With respect to the signals of the Cp-ligand in  $\text{Cp}_2\text{HfCl}_2$  complex [19].

$^1\text{H}$  and  $^{13}\text{C}$  resonances could be given only on the basis of a suitable combination of 2D correlation spectroscopy techniques. The signals of separate protons in the PMR spectra were assigned on the basis of the relative chemical shifts and spin–spin interactions, as well as  $^1\text{H}$ – $^1\text{H}$  and  $^1\text{H}$ – $^{13}\text{C}$  correlation experiments. The assignment of the  $^{13}\text{C}$  resonances was made from the relative chemical shifts, spin–spin splittings observed in the proton coupled  $^{13}\text{C}$  spectra,  $^1\text{H}$ – $^{13}\text{C}$ , and  $^{13}\text{C}$ – $^{13}\text{C}$  correlation experiments. The NMR data and their interpretation are shown in Table 1.

Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show pronounced downfield shifts of the resonance signals of the C2 directly bonded to the metallocene through the oxygen bridge, and H2. As far as other atoms of the alicyclic framework are concerned, the influence of coordination on the position of their resonance signals is less significant and decreases with the increase of their distance from the coordination point.

The experiments were designed in a way that enables statistical treatment of the data in order to find out the influence of the studied variables (polymerisation temperature and pressure) on the catalyst performance and the polymer properties. Table 2 shows the catalytic activity and characteristics of resulting polymers, such as melting temperature ( $T_m$ ), crystallinity degree ( $x_c$ ), weight-average molecular weight

( $M_w$ ) and polydispersity ( $M_w/M_n$ ), obtained using the catalytic system under investigation.

Fig. 1 shows the dependence of polymerisation rate from the reaction time for the experiments 1–5. The highest polymer yield was obtained at 100 °C in the absence of  $\text{H}_2$  due to higher initial polymerisation rate, i.e. higher initial concentration of the active centres. Essentially, the reaction is practically completed during the first 30 min in all cases, but the experiment 4, when the system remains still active after 1 h. However, the reaction was terminated for the uniformity of experiments.

The statistical treatment was realised using a program Statistica for MS Windows. A model obtained for the catalytic activity ( $A$ ) is described by Eq. (1).

$$A = -482.5T^2 + 297.5T - 216.5T[\text{H}_2] - 600.5[\text{H}_2] + 1566 \quad (\text{correlation index } R^2 = 0.99). \quad (1)$$

A plot of  $A = f(T; [\text{H}_2])$  using normalised variables gives a model surface of the activity versus polymerisation temperature and hydrogen concentration (see Fig. 2a).

The same procedure was also applied for weight-average molecular weight of the obtained polyethylene. The result is

Table 2  
 Design of experiments and results of ethylene polymerisation with  $\text{Cp}_2\text{Hf}(\text{OFI})_2/\text{MAO}^a$

Experiment	$T_p^b$ (°C)	$\text{H}_2^b$ (molar%)	Activity (kg PE/[Hf] h)	$T_m$ (°C)	$x_c$ (%)	$M_w$ ( $\times 10^{-3}$ ) (g/mol)	$M_w/M_n$
1	100 (+1)	7 (+1)	564	134	81	44	2.1
2	100 (+1)	0 (-1)	2198	134	67	135	2.2
3	50 (-1)	7 (+1)	402	135	75	118	2.0
4	50 (-1)	0 (-1)	1170	133	54	842	2.6
5	75 (0)	3.5 (0)	1556	135	67	237	2.3
6	75 (0)	3.5 (0)	1320	n.d.	n.d.	187	2.3
7	75 (0)	3.5 (0)	1680	n.d.	n.d.	211	2.3

<sup>a</sup> Polymerisation conditions: toluene = 100 ml; [Hf] =  $5 \times 10^{-5}$  mol; [Al]/[Hf] = 2000; ethylene pressure = 2 bar.

<sup>b</sup> These independent variables were normalised for statistical treatment as shown in parentheses.

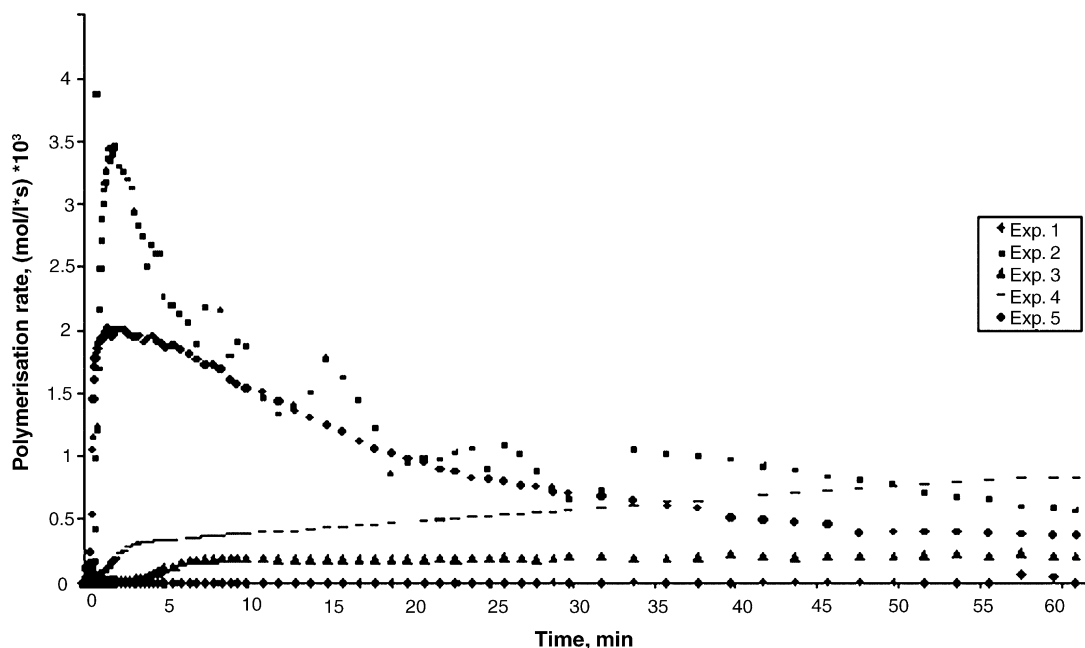


Fig. 1. Polymerisation rate vs. time for the experiments 1–5 (see Table 2).

expressed by Eq. (2).

$$M_w = -195.25T - 203.75[H_2] + 158.25T[H_2] + 264.5 \quad (2)$$

( $R^2 = 0.99$ ).

Similarly, the model surface of weight-average molecular weight versus polymerisation conditions is shown in Fig. 2b.

We tried to derive similar statistical models for other polymer properties like melt temperature ( $T_m$ ), crystallinity degree ( $x_c$ ) and polydispersity ( $M_w/M_n$ ), however, the results were unsatisfactory. The above could be explained by a preferential dependence of the parameters in question on a microstructure of the macromolecules than on the polymerisation conditions.

Previously [13], we studied the polymerisation of ethylene with a tricyclic alcoholate of hafnocene  $Cp_2Hf(OMAd)_2$  (where OMAd means a deprotonated moiety of 2-methyladamantan-2-ol) in comparison with the hafnocene dichloride. Since the experimental conditions used in the present study are analogous to those in [13], we are able to compare the catalytic activity and  $M_w$  of resulting polymers for all three cases. The model surfaces could be used to understand the performance of the systems under discussion in the studied range of variables.

Fig. 3a clearly shows a different character of the dependence of activity on the  $T_p$  and  $[H_2]$  in the cases of  $Cp_2Hf(OMAd)_2$  and  $Cp_2HfCl_2$  from one hand, and  $Cp_2Hf(OFl)_2$  from the other hand. The model surfaces of the former two systems have a maximum, while in the latter case

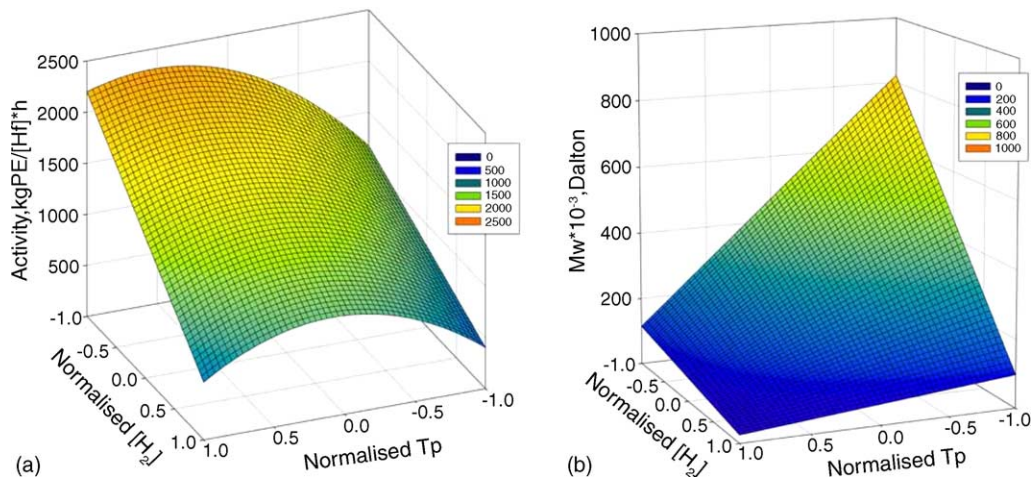


Fig. 2. Graphic representation of the catalytic activity (a) and  $M_w$  (b) models for  $Cp_2Hf(OFl)_2/MAO$  system.



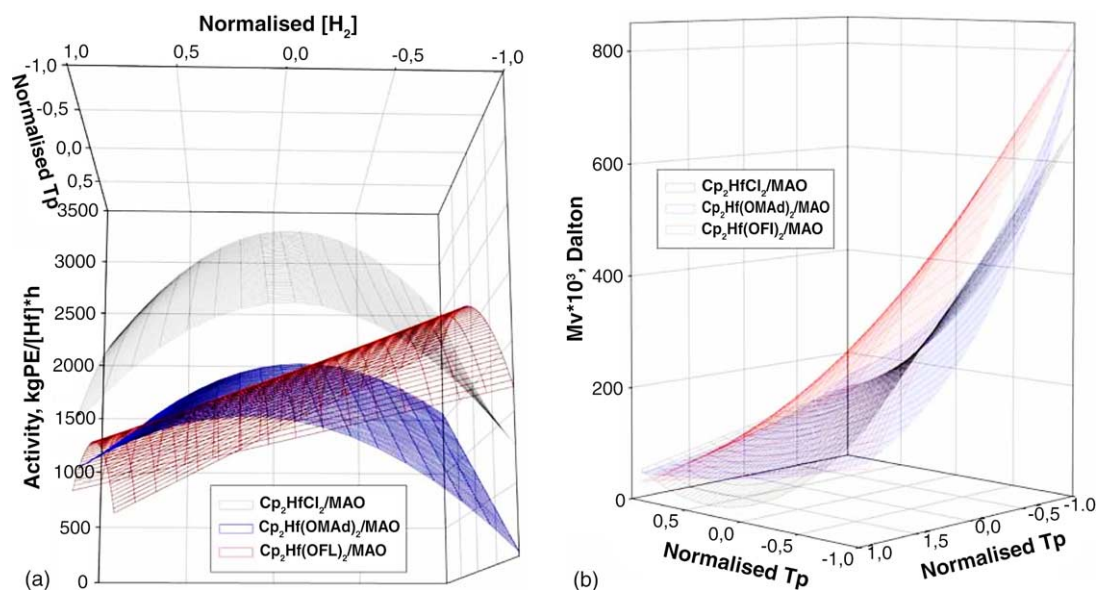


Fig. 3. Model surfaces of the catalytic activity (a) and  $M_w$  (b) for  $Cp_2HfX_2/MAO$  system.

the activity is continuously growing with the increase of  $T_p$ . In the lower temperature interval the hafnocene dichloride is less active than the dichloride and has nearly the same activity as the diadamantanolate. In the middle temperature range the activity of new catalyst occupies an intermediate position. At higher temperatures, it becomes considerably higher than the activity of two reference catalysts. The observed behaviour is evidently connected to the following factors. From one hand, the difencholates of hafnocene is a highly thermally stable compound. From the other hand, a high steric shielding ability of the  $\sigma$ -bonded alcoholato-ligand counteracts a deactivation of the catalyst.

The dependence of the activity from hydrogen concentration is less pronounced in all cases. Hydrogen is usually added to the polymerisation system as a molecular weight moderator and stabiliser of the polymerisation process. However, in general, the presence of H<sub>2</sub> reduces the activity of the catalyst. For the hafnocene dichloride, the dependence of activity from [H<sub>2</sub>] is nearly the same through the temperature range of 50–100 °C and has a maximum in the region of 3.5% H<sub>2</sub>. The behaviour of Cp<sub>2</sub>Hf(OMAd)<sub>2</sub> is slightly different: at lower temperatures the dependence is similar to that of the dichloride, then at  $T_p > 60$  °C the addition of hydrogen favours the increase in catalytic activity. The activity of Cp<sub>2</sub>Hf(OFl)<sub>2</sub> catalyst uniformly decreases with the increase of [H<sub>2</sub>] in the whole range of temperatures in question.

A comparison of the dependencies of the  $M_w$  of the polyethylene on the  $T_p$  and [H<sub>2</sub>] is shown in Fig. 3b. The surfaces are similar in all cases. As expected, they demonstrate a diminution of the  $M_w$  both with the increase of temperature and hydrogen concentration. At the same time, the difencholates of hafnocene always produces polyethylene with the highest molecular weight among the catalysts under discussion. This effect could be explained as a result

of growing steric shielding ability of the ligands in the row  $-OFl > -OMAd > -Cl$  that reduces the probability of chain termination and chain transfer reactions.

Thus, we analysed the dependencies of the catalytic activity and  $M_w$  on the independent variables of the process ( $T_p$  and [H<sub>2</sub>]) for ethylene polymerisation with different  $\sigma$ -substituted hafnocene/MAO systems. In turn, to a certain extent the  $M_w$  is also dependent on the activity. Hence, it is interesting to analyse a function of  $M_w = f(A; T_p; [H_2])$ . Graphic representation of such a function will require a 4D plot that can not be produced, so we will visualise and analyse spatial sections of this function  $M_w = f_1(A; T_p)$  (Fig. 4) and  $M_w = f_2(A; [H_2])$  (Fig. 5).

The  $M_w = f_1(A; T_p)$  pattern clearly demonstrates a difference between the Cp<sub>2</sub>Hf(OFl)<sub>2</sub> catalyst and two reference hafnocenes. For chloro- and methyladamantanolate derivatives the activity and temperature dependence of the  $M_w$  is represented as a paraboloid (Fig. 4a and b), while the same plot for the difencholates complex appears as only one arc of the paraboloid (Fig. 4c). Thus, the analysis of the former two surfaces indicates that Cp<sub>2</sub>HfCl<sub>2</sub>/MAO and Cp<sub>2</sub>Hf(OMAd)<sub>2</sub>/MAO catalytic systems have a maximum of activity in a median range of [H<sub>2</sub>], i.e. 3.5% is an optimal hydrogen concentration for the above catalysts. Whereas for the Cp<sub>2</sub>Hf(OFl)<sub>2</sub>/MAO system a maximum of activity has not yet been achieved. It is also interesting to note, a range of  $M_w$  for polyethylenes obtained at the same temperature at the starting and final values of the hydrogen concentration, i.e.  $\Delta M_w = M_w([H_2] = 0\%) - M_w([H_2] = 7\%)$  has a maximum width at low temperatures, and contracts significantly at the higher ones.

In the case of  $M_w = f_2(A; [H_2])$  pattern (Fig. 5) the surfaces are quite different. For the Cp<sub>2</sub>Hf(OMAd)<sub>2</sub> the dependence is a paraboloid arc without extreme values (Fig. 5b), moreover,

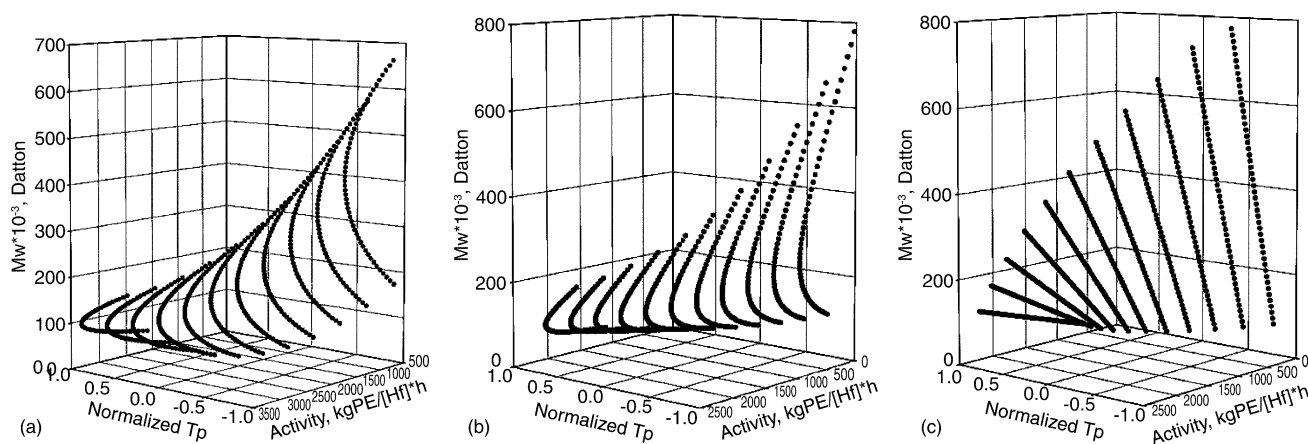


Fig. 4. Dependence of  $M_w$  from the catalytic activity and  $T_p$  for  $Cp_2HfCl_2/MAO$  (a);  $Cp_2Hf(OMAd)_2/MAO$  (b);  $Cp_2Hf(OFl)_2/MAO$  (c) systems.

Table 3  
Ethylene polymerisation in scaled-up conditions

Catalyst	Activity (kg PE/[Hf] h)	$M_w$ ( $\times 10^3$ )
$Cp_2HfCl_2$	1892	40
$Cp_2Hf(OFl)_2$	1071	73

the catalytic activity lowers less significantly with an increase of  $[H_2]$  than that of the other two complexes. The pattern for  $Cp_2HfCl_2/MAO$  system (Fig. 5a) reveals a minimum of  $M_w$  in the higher ranges of  $T_p$  and  $[H_2]$ , as well as maxima of the catalytic activity at hydrogen concentrations of 1.75% and 5.25%. As the concentration of hydrogen increases from 0% to 7%, the difenholate of hafnocene (Fig. 5c) demonstrates a gradual shift of the catalytic activity maximum from 75 down to 50 °C, respectively.

Ethylene polymerisation tests in a scaled-up autoclave at 1500 kPa were realised at derived optimal values of hydrogen concentration (3.3%) and the reaction temperature (70 °C), the results are presented in Table 3.

These experiments demonstrate a tendency similar to that observed at lower pressures, the activity of  $Cp_2Hf(OFl)_2$  catalyst is slightly lower with respect to the dichloride complex,

while the molecular weight of the polyethylene produced is considerably higher.

We discussed above the catalytic performance of new system  $Cp_2Hf(OFl)_2$  in the homogeneous ethylene polymerisation activated by MAO in comparison with a traditional hafnocene dichloride and another bridged alicyclic alcoholate  $Cp_2Hf(OMAd)_2$ , obtained by us earlier. Nevertheless, the experiments were realised in equal conditions, both the polymerisation reaction and properties of the resulting polymer were found to be rather different. These differences could only be explained by assuming an active role of the voluminous  $\sigma$ -bonded ligand. On the analogy of propylene polymerisation with previously described  $Ind_2ZrCl(OFl)/MAO$  system [14], a heteronuclear active site  $[Cp_2HfMe]^+[FIO-MAO]^-$  has to be considered, where the fencho-lato-ligand is re-coordinated to the co-catalyst. Therefore, the voluminous bridged alicyclic ligand, possessing all three dimensions comparable to those of the rest of the metallocene complex, will be situated in an immediate proximity from the transition metal active centre. This is the case where the  $\sigma$ -ligand could really influence the polymerisation process, whereas in other works dealing with the influence of  $\sigma$ -bonded ligands [5–10], the latter was always much

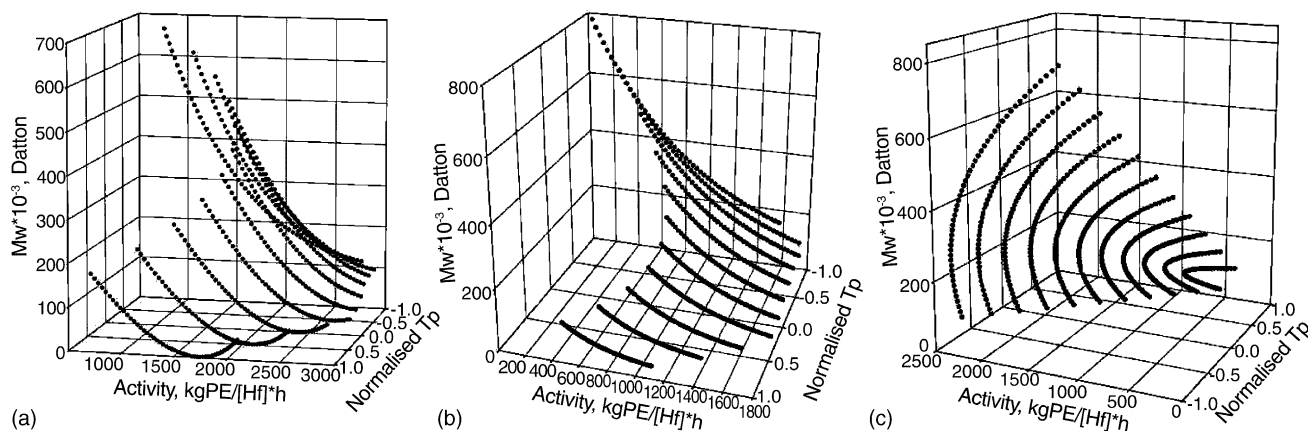


Fig. 5. Dependence of  $M_w$  from the catalytic activity and  $[H_2]$  for  $Cp_2HfCl_2/MAO$  (a);  $Cp_2Hf(OMAd)_2/MAO$  (b);  $Cp_2Hf(OFl)_2/MAO$  (c) systems.

smaller than the metallocene core in one, two or all three dimensions.

#### 4. Conclusions

Results of the present investigation provide additional confirmation of the fact that  $\sigma$ -bonded ligands are not indifferent constituents of metallocene coordination compounds, the catalysts of homogeneous  $\alpha$ -olefin polymerisation, as it has been commonly supposed. When the dimensions of these ligands become commensurable with those of the transition metal active centre, they are able to influence both the polymerisation process and properties of the final polymer. Therefore, the present work together with previous ones [11–14] demonstrate that jointly with an appropriate choice of the transition metal and  $\pi$ -bonded aromatic ligands, a fine tuning of metallocene catalytic systems may also be realised via tailoring of suitable  $\sigma$ -bonded sterically shielding ligands.

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