

# Extremely active polymerizations of propene by bisindenylzirconocenes and tetra(pentafluorophenyl)-borate

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Dedicated to Wittko Francke on the occasion of his 60th birthday.

## Abstract

The homogeneous homopolymerization of propene was conducted with the two catalyst precursors  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrBz}_2$  (**1**) and  $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrBz}_2$  (**2**) and triphenylmethyltetrakis(pentafluorophenyl)borate  $[\text{C}(\text{CH}_3)_3][\text{B}(\text{C}_6\text{F}_5)_4]$  (**3**) as cocatalyst. After synthesizing the dibenzyl compounds from their dichloride derivatives the catalyst system (**1**)/(**3**) was optimized in respect to the catalyst/cocatalyst ratio and the amount of tri(isobutyl) aluminum (TIBA).

The polymerization behavior of the catalyst system (**2**)/(**3**) is investigated using a central composite experimental design. In this design the dependence of the polymer properties on temperature, catalyst and monomer concentration are modeled.

The dibenzyl compound (**2**) shows extremely high catalytic activities of 600 000 kg PP/mol<sub>Zr</sub> h mol<sub>p</sub>. The polymers produced with this catalyst exhibit very high melting points and molecular weights. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Homopolymerization; Tetra(pentafluorophenyl)borate; Bisindenylzirconocene

## 1. Introduction

A lot of investigation has been carried out in order to optimize the counteranion in the polymerization process with metallocene catalysts [1–3]. Although the well known methylaluminoxane (MAO) is used in industrial processes a number of other cocatalysts have been investigated recently. Especially some larger boron organic compounds seem to fulfil their role as non-coordinating, non-nucleophilic counteranion to the active cationic species very well, as shown by studies published by Bochmann et al. [4,5], Marks et al. [6] and Chien et al. [7,8]. One of the most promising compounds in this matter is the trisphenylmethyltetrakis(pentafluorophenyl)borate  $[\text{C}(\text{CH}_3)_3][\text{B}(\text{C}_6\text{F}_5)_4]$  (**3**) which was synthesized by Chien et al. [7] for the first time.

We were interested in the outcome of the combination of (**3**) with the most efficient ansa-metallocenes for the polymerization of propylene, the dimethylsilyl-bridged zirconocene-bisindenylsystems. The catalyst  $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrCl}_2/\text{MAO}$  is known to be highly active in producing polypropylene with a very high isotacticity, a high melting point and high molecular weight [9].

It is interesting to explore if these characteristics of the catalyst can only be achieved in combination with MAO or if this performance is observable with another cocatalyst, too. Hahn and Fink [10] published results reporting on the polymerization of propylene they carried out with the basic alkylated system of the bridged bisindenyl zirconocene compounds  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$  and Brintzinger and Mühlhaupt found that an activated cationic  $\text{Me}_2\text{Si}(2\text{-Me-4,5-Bzo-Ind})_2\text{ZrX}_2$  in combination with different cocatalysts, e.g. (**3**) were capable of polymerizing propylene [11].

The fact that high polymerization activities can be achieved with zirconocene dibenzyls/ $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$  has been reported by Bochmann [12].

Since there is a lack of the abstracting and alkylating properties of MAO in the solution the zirconocene dichlorides have to be alkylated beforehand, so that either the dimethyl or the dibenzyl compounds of the metallocene are used in the polymerization.

Jordan et al. [13] found that the dibenzyl species are stabilized by a coordination of the ipso C-atom of the benzyl group to the zircononium center, therefore we benzylated the dichlorides of the metallocenes used for our

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polymerizations. The synthesis of the metallocene  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrBz}_2$  (**1**) has been reported before [14].

There are results that state that an in situ alkylating mechanism [15] with the tri(isobutyl)aluminum (TIBA) used in the polymerization as a scavenger is possible as well. In this case the dichlorides are used in the polymerization solution directly and they are alkylated by TIBA in a similar way as by MAO.

## 2. Experimental

### 2.1. Synthesis of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrBz}_2$ (**1**)

$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  (252 mg; 0.56 mmol) and  $\text{K}(\text{C}_6\text{H}_5\text{CH}_2)$  (228.9 mg; 1.76 mmol) were dissolved in 24 ml of dry toluene and stirred at room temperature for 4 h. The resulting suspension was filtered and the toluene was removed from the filtrate under vacuum. An orange/red solid was observed. It was redissolved in 7 ml of toluene and precipitated with 20 ml pentane added successively.

Filtering of the precipitate and drying under vacuum yielded 78.4 mg (0.14 mmol) of compound (**1**).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.06–7.47 (m, 12H, *m*-H and  $\text{C}_6$ ), 6.86 (d, 2H, *p*-H, Ph), 6.66 (d, 4H, *o*-H, Ph), 5.88 (d, 2H,  $\text{C}_5$ ), 5.61 (d, 2H,  $\text{C}_5$ ), 0.90 (s, 6H, Si- $\text{CH}_3$ ), 0.58 (d, 2H, Zr- $\text{CH}_2$ ), –0.51 (d, 2H, Zr- $\text{CH}_2$ )

### 2.2. Synthesis of $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrBz}_2$ (**2**)

$\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrCl}_2$  (294.4 mg; 0.47 mmol) and  $\text{K}(\text{C}_6\text{H}_5\text{CH}_2)$  (154.4 mg; 1.19 mmol) were dissolved in 50 ml of dry toluene and stirred at room temperature for 24 h. The resulting suspension was filtered and the toluene was removed under vacuum from the filtrate. A brownish solid was observed. It was partly redissolved in 30 ml of toluene and filtered again.

Addition of 30 ml of dry pentane resulted in precipitation of a brown solid.

Filtering of the precipitate and drying under vacuum yielded 104.3 mg (0.14 mmol) of compound (**2**).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.03–7.61 (m, 16H,  $\text{C}_6$  and 4-Ph), 6.51–6.60 (m, 6H, H-Ph), 6.2 (d, 2H, H, Ph), 6.13 (d, 2H, H, Ph), 5.90 (s, 2H,  $\text{C}_5$ ), 2.07 (s, 6H, 2- $\text{CH}_3$ ), 1.15 (s, 6H, Si- $\text{CH}_3$ ), 0.75 (d, 2H, Zr- $\text{CH}_2$ ), 0.64 (d, 2H, Zr- $\text{CH}_2$ ).

Since the yield of the synthesis of the zirconocene dibenzyls are very low, no  $^{13}\text{C-NMR}$  spectroscopy or elemental analysis were carried out.

All procedures were carried out in an argon atmosphere. Toluene and pentane were dried over sodium/potassium or by passage through columns with Cu catalyst (BASF R3-11) and molecular sieve of 4 Å,  $\text{CDCl}_3$  was dried over molecular sieve 4 Å.

A typical polymerization was performed in a 1 l Büchi glass autoclave which was charged successively with 200 ml of toluene, a TIBA solution ( $1 \times 10^{-3}$  mol/l) and monomer (1.3 mol/l).

To polymerize at a constant monomer concentration the pressure was adapted to the different temperatures.

The reaction was initiated by injecting the zirconocene ( $2.5 \times 10^{-7}$  mol/l) and terminated by the addition of ethanol. The products were washed with ethanol/HCl, neutralized and dried in vacuum.

Monomer consumption was monitored and recorded with a mass flow controller Brooks 5850 TR.

The polymerizations 1–15 have been repeated once and the general error margin is within 15%.

The zirconocene dichlorides were either supplied by the former Hoechst AG (**2**) or synthesized in our group (**1**) [16]. MAO and TIBA were purchased from Witco.

Viscosimetry was carried out with an Ubbelohde capillary 0a ( $K = 0.005$ ). Measuring conditions were 135°C/decahydronaphthalene for PP. The Mark–Houwink constants ( $k = 0.0238 \text{ ml g}^{-1}$ ,  $a = 0.725$ , PP have been reported elsewhere [17].

Differential scanning calorimetry analyses were performed on a Mettler–Toledo DSC 821e instrument (heating rate 20°C min $^{-1}$ ). The results of the second runs are reported.

Catalyst  $^1\text{H-NMR}$  spectra were recorded at room temperature on an AC 100 Bruker spectrometer.

Polymer  $^{13}\text{C-NMR}$  spectra were recorded at 100°C on a 300 MHz Bruker MSL 300 spectrometer. The assignment of the pentads of the polypropene is reported in the literature [18]. Hexachlorobutadien and deuterated tetrachloroethane were used as solvents.

## 3. Results and discussion

The first goal we had was to optimize the polymerization conditions and we chose the basic system (**1**) to investigate it concerning the amount of TIBA and the ratio between the cocatalyst and the catalyst.

### 3.1. Stability of the polymerization with (**1**) as precursor

Although in the literature problems in the reproduction of results are mentioned [9] using systems with the compound (**3**) as cocatalyst we were able to create a fairly stable system when we used the prebenzylated compounds (**1**) and (**2**) as catalysts.

After a short time of inhibition the monomer consumption increases until it reaches a constant value. In Fig. 1 this value is reached after 6 min and it stays more or less constant until the reaction is terminated. The incubation time is probably due to the inertia of the mass flow controller.

### 3.2. Polymerization with (**1**) as catalyst precursor

#### 3.2.1. Investigation of the amount of TIBA

The influence of the amount of the scavenger TIBA in respect to the activity of the polymerization and some polymer characteristics were investigated.

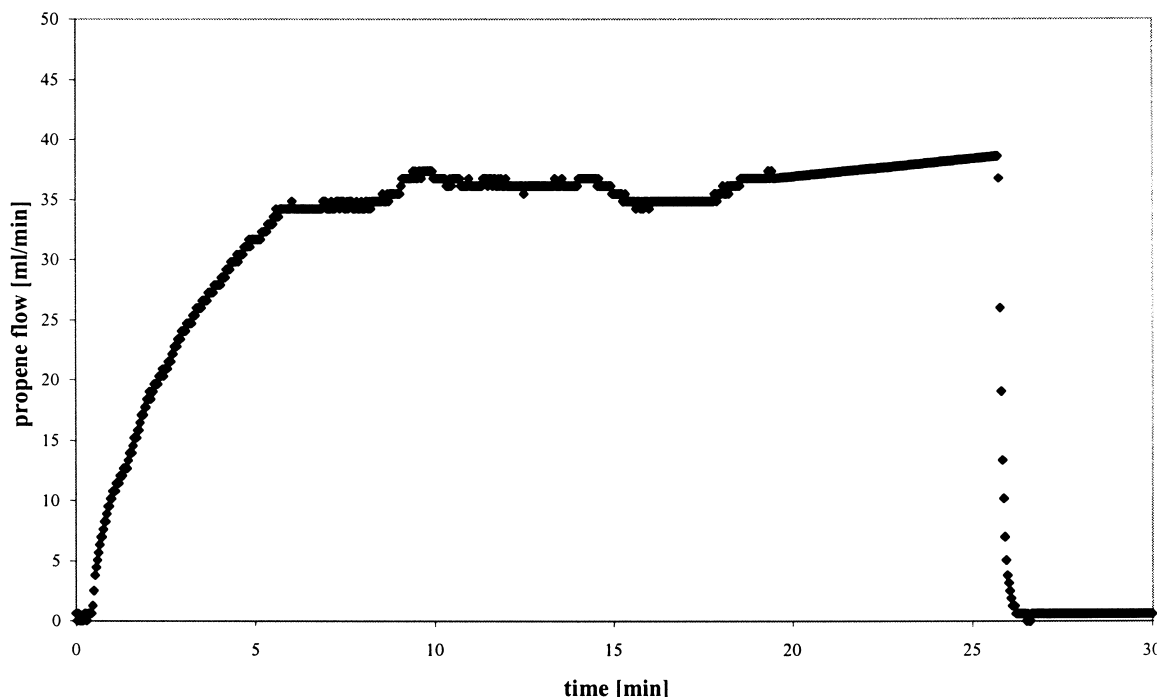


Fig. 1. Mass flow graph of the polymerization of propene by catalyst (1)/(3). Polymerization conditions: 200 ml toluene; catalyst conc.,  $2.46 \times 10^{-7}$ ; cocatalyst/catalyst ratio, 3.1; propene conc., 1.3 mol/l; TIBA conc.,  $1.03 \times 10^{-3}$  mol/l; temp., 30°C; time, 30 min.

From Table 1 it can be seen that the amount of TIBA has no influence on the melting point ( $T_m$ ), the isotacticity or the viscosimetric molecular weight of the resulting polymer.

The values of these polymer characteristics match the polymer produced with MAO as cocatalyst very well [19].

Interesting is the dependency of the activity on the amount of TIBA — the highest activity is observed with 0.199 mmol TIBA in the 200 ml reaction volume of toluene.

After the activity reaches this maximum a decrease in the reaction rate is observable, so that a larger amount of TIBA seems to slow down the polymerization reaction (Fig. 2).

Another remarkable result that we found is that the amount of TIBA does not have an impact on the molecular weight.

In the literature it is known that the amount of aluminum compounds used as a scavenger does have an influence on

the activity and the molecular weight and that an increase of their concentration results in a decrease in the molecular weight of the polymer produced [20]. An often used explanation for this behavior is the influence on the equilibrium between active polymerization catalyst species and inactive — probably aluminum blocked — systems of the precursor. An increase in the scavenger concentration would increase the number of inactive centers and therefore — taking into account  $\beta$ -hydride elimination which can occur at both kinds of centers — the molecular weight would drop.

Additionally an enhanced chain transfer from the zirconocene center to the aluminum can be proposed with a higher TIBA concentration.

This behavior is not observable for TIBA in the area of concentration investigated. So the TIBA species does

Table 1

Influence of TIBA on the polymerization of propene by catalyst (1)/(3)

Polymerization conditions: 200 ml toluene; catalyst conc.,  $9.75 \times 10^{-7}$  mol/l; cocatalyst/catalyst ratio, 1.54; propene conc., 1.3 mol/l; temp., 30°C

Run number	$T_p^a$ (min)	Amount of TIBA (mmol)	Activity (kg PP/(mol <sub>Zr</sub> mol/l <sub>p</sub> h))	$T_m$ (°C)	Isotacticity (%mmmm)	$M_\eta$ (kg/mol)
1	50	0.099	0			
2	50	0.148	22 600	145	93	90 000
3	15	0.158	46 500	145	95	80 000
4	15	0.199	61 000	145	94	96 000
5	15	0.396	46 600	146	94	89 000
6	15	0.992	25 100	146	94	109 000

<sup>a</sup>  $T_p$ , time of polymerization.

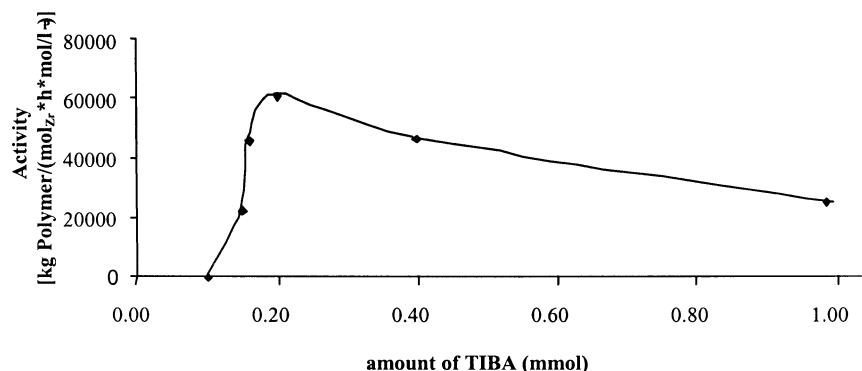


Fig. 2. Activity of the polymerization of propene with catalyst (1)/(3) vs amount of TIBA. Polymerization conditions see Table 1.

not seem to have such a large influence on the mentioned equilibrium or the  $\beta$ -hydride elimination is not the dominating chain termination reaction.

Additionally the lacking influence on the molecular weight indicates again that the TIBA compound is a poor transfer agent, because alkyl or hydride transfer reactions terminate the growth of the single polymer chain.

### 3.2.2. Investigation of the cocatalyst/catalyst ratio

The activities we found are extremely high compared to the corresponding dichloride compound. The activity found for the catalyst  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$  under the same conditions is 28 000 kg polymer/(mol<sub>Zr</sub> mol/l<sub>p</sub> h) [15].

The catalytic species seems to be dependent on cocatalyst/catalyst ratio (Table 2). With a ratio of three a polymer with a much higher melting point and a very high molecular weight is produced. This molecular weight is nearly ten times as high as the polymer produced with a catalyst system with a ratio of 1.5 and almost seven times as high as polymer made with a value of the cocatalyst/catalyst ratio of 5.2.

For the high melting point observed for the polymer produced with a ratio of three a sufficient explanation cannot be given yet.

Nevertheless the observed results show that the borate seems to have an influence on the active species in which more than one molecule of cocatalyst is taking part. An

explanation for this behavior could be that the active species is stabilized by more than one borate anions or that the abstracting ability of the “trityl” cation is not efficient enough to activate all zirconocene dibenzyls and therefore an excess of cocatalyst is needed.

### 3.3. Polymerization with (2) as catalyst precursor

#### 3.3.1. Determination of the activation energy in the polymerization of propene

To determine the activation energy in the polymerization with catalyst (2) polymerizations were carried out at different temperatures (Table 3).

From the activities, the Arrhenius plot (Fig. 3) can be observed and the value of the activation energy for the system (2)/(3) is now easily calculated to be 50 KJ/mol.

This value is slightly lower than the activation energies calculated for dimethylsilyl bridged zirconocenes activated by MAO [21].

The observed molecular masses and activities are extremely high, the polymerization at 45°C with an activity of 600 000 kg PP/mol<sub>Zr</sub> h mol<sub>p</sub> is one of the highest ever reported for propene.

It is interesting to note though that the polymerization with this catalyst system at 60°C is not active at all. Therefore, these systems seem to be very temperature sensitive which makes them difficult to employ in industrial

Table 2

Polymerization results of an investigation of the polymerization of propene by catalyst (1)/(3)

Polymerization conditions: 200 ml toluene; catalyst conc.,  $9.75 \times 10^{-7}$  mol/l; TIBA conc.,  $1.03 \times 10^{-3}$  mol/l; propene conc., 1.3 mol/l; temp., 30°C

Run number	$T_p^a$ (min)	Amount of TIBA (mmol)	Activity (kg PP/(mol <sub>Zr</sub> mol/l <sub>p</sub> 200 h))	$T_m$ (°C)	Isotacticity (%mmmm)	$M_n$ (kg/mol)
7	30	1.03	2400	146	93	50 000
8	20	1.55	181 000	144	94.5	76 000
9	20	3.11	211 500	163	95	677 000
10	30	5.2	215 000	145	94	96 000
11	30	20.7	189 000	146	94	73 000

<sup>a</sup>  $T_p$ , time of polymerization.

Table 3

Polymerization results of the polymerization of propene with (2)/(3)

Polymerization conditions: 200 ml toluene; propene conc., 1.3 mol/l; cocatalyst/catalyst ratio, 3; TIBA conc.,  $1 \times 10^{-3}$  mol/l

Run number	Catalyst conc. (mol/l) $\times 10^{-7}$	$T_p^a$ (min)	Temp. ( $^{\circ}$ C)	Activity (kg PP/ (mol <sub>Zr</sub> mol <sub>P</sub> h))	$T_m$ ( $^{\circ}$ C)	Molar mass (g/mol)
12	10	30	0	28 000	164	4 400 000
13	7.4	15	15	100 000	165	3 500 000
14	5	15	30	310 000	164	1 000 000
15	5	10	45	600 000	168	300 000

<sup>a</sup>  $T_p$ , time of polymerization.

applications. An explanation for this behavior could be the increased Lewis-acidity of the active center that results in the lacking stabilization by the MAO counter anion if using the borate anion in the polymerization process.

If MAO is used as the cocatalyst at a polymerization temperature of  $70^{\circ}$ C a very high activity is reported in the literature [9].

The molecular masses are extremely high, too, the 4.4 mio g/mol for the polymer produced at  $0^{\circ}$ C are the highest value ever found for this polymer.

The melting points ( $164$ – $165^{\circ}$ C) are in the same region as the melting points for polypropenes made by this catalyst precursor and MAO as cocatalyst and in this chosen interval the melting points seem to be independent of the temperature. The high value for the melting point of the polymer produced at  $45^{\circ}$ C ( $168^{\circ}$ C) can not be explained yet, it is unusual because the expected trend would be an decrease of the melting point with an increase in the temperature of the polymerization.

### 3.4. Central composite design

We used an empirical model to determine the influence of three factors (temperature, concentration of monomer and concentration of catalyst) on several target properties ( $\Psi$ ) of the polymerization and the polymers, respectively.

By carrying out a small number of planned experiments this method has the advantage of a reduced number of experiments and the correlation between different experimental conditions [22].

The effect of the factors can be visualized by a response surface plot, a three-dimensional plot showing the effects of two factors while the third is kept at a constant value. This surface is determined by the projection of nine experimental values in the plane set up by the two factors on the  $x$ - and  $y$ -axis.

The experimental design (Fig. 4) is evaluated by the software program Statistica<sup>®</sup>.

The used design consists of 16 runs, the central run is repeated to determine the statistical error. This error is about 20% for the polymerization activity and the molar masses and about 2% for the melting point.

The function  $\Psi$  can be described as a development in a series which is cut off after the square member:

$$\Psi = [k_1 T + k_2 c_{\text{mon}} + k_3 c_{\text{cat}}] + [k_4 T c_{\text{mon}} + k_5 T c_{\text{cat}} + k_6 c_{\text{mon}} c_{\text{cat}}] + [k_7 T^2 + k_8 c_{\text{mon}}^2 + k_9 c_{\text{cat}}^2] + \text{const.}$$

where  $\Psi$  is the target function;  $k_i$  the coefficients of the effects;  $T$ ,  $c_{\text{mon}}$ , and  $c_{\text{cat}}$  are the factors such as temperature, concentration of the monomer, and concentration of the catalyst, respectively.

The validity of the applied mathematical model for the experimental data can be checked by a comparison of the observed data with the calculated values from the model (Tables 4 and 5). The best fit is achieved for the melting points as target polymer property of the polymer.

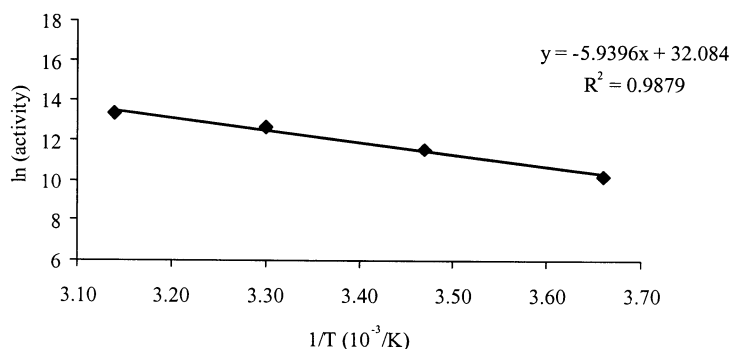


Fig. 3. Arrhenius plot for the polymerization of propene with (2)/(3).

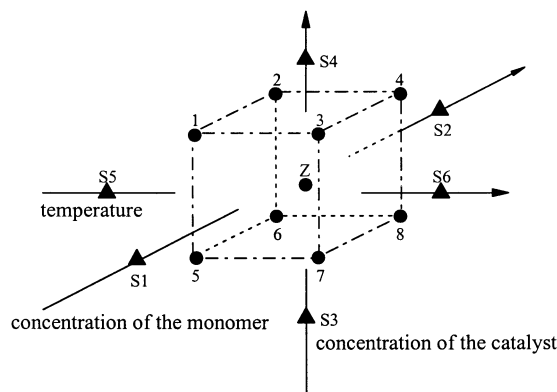


Fig. 4. Schematic draw of the experimental design.

Target functions of the response surface plots of the statistical evaluation.

(a) Catalyst potential

$$\Psi = [-5.8T - 165c_{\text{mon}} - 518\,678\,371c_{\text{cat}}] + [2.31Tc_{\text{mon}} + 2\,603\,113Tc_{\text{cat}} + 215\,431\,708c_{\text{mon}}c_{\text{cat}}] + [0.004T^2 + 8.64c_{\text{mon}}^2 + 89\,717\,456\,305\,40c_{\text{cat}}^2] + 322$$

(b) Melting temperature

$$\Psi = [-0.22T + 11.1c_{\text{mon}} + 34\,889\,061c_{\text{cat}}] + [0.04Tc_{\text{mon}} + 172\,043Tc_{\text{cat}} - 16\,666\,666c_{\text{mon}}c_{\text{cat}}] - [0.003T^2 + 1.0c_{\text{mon}}^2 + 4\,756\,463\,705\,058c_{\text{cat}}^2] + 149$$

Table 4

Conditions for the central composite design

Further conditions: cocatalyst/catalyst ratio, 3; TIBA conc., 0.001 mol/l; time, 10–60 min

Run	Temperature (°C)	Catalyst conc. (mol/l)	Monomer conc. (mol/l)
Z	22.5	$5.50 \times 10^{-7}$	2.1
Z	22.5	$5.50 \times 10^{-7}$	2.1
S1	22.5	$5.50 \times 10^{-7}$	1.4
S2	22.5	$5.50 \times 10^{-7}$	2.8
S3	22.5	$1.00 \times 10^{-7}$	2.1
S4	22.5	$1.20 \times 10^{-7}$	2.1
S5	-3.5	$5.50 \times 10^{-7}$	2.1
S6	48.5	$5.50 \times 10^{-7}$	2.1
1	7.0	$9.25 \times 10^{-7}$	1.7
2	7.0	$9.25 \times 10^{-7}$	2.5
3	38.0	$9.25 \times 10^{-7}$	1.7
4	38.0	$9.25 \times 10^{-7}$	2.5
5	7.0	$1.75 \times 10^{-7}$	1.7
6	7.0	$1.75 \times 10^{-7}$	2.5
7	38.0	$1.75 \times 10^{-7}$	1.7
8	38.0	$1.75 \times 10^{-7}$	2.5

(c) Molar masses

$$\Psi = [-108\,431T + 4\,438\,947c_{\text{mon}} + 5\,445\,011\,635\,741c_{\text{cat}}] + [38\,870Tc_{\text{mon}} + 27\,698\,924\,731Tc_{\text{cat}} - 2\,410\,000\,000\,000c_{\text{mon}}c_{\text{cat}}] - [771T^2 + 1\,038\,304c_{\text{mon}}^2 + 1\,525\,916\,805\,439\,569\,000c_{\text{cat}}^2] - 1\,516\,395$$

3.5. Molecular masses of the polymers

In the investigated area the molecular masses of the polypropenes are dependent on the temperature of the polymerization.

In Fig. 5 it can be seen that a decrease of the temperature results in an increase of the molecular mass of the polymer. This result was expected since this behavior can be observed for other systems, too [23]. The dependence from the concentration of the catalyst that can be observed from Fig. 5 is within the statistical error and therefore not relevant under the chosen conditions.

The molar masses are very high again and go up to values larger than  $4 \times 10^6$  g/mol.

3.6. Melting points of the polymers

In the investigated area of the polymerization conditions the melting point of the polymers depends only on the temperature, too. This dependence is shown in Fig. 6 in which the melting point increases with decreasing polymerization temperature. An explanation for this behavior has been given before [23], the number of stereo- and regio-errors drops with decreasing polymerization temperature.

The usual behavior of single site catalysts in the polymerization of propene is that the melting point increases with increasing monomer concentration but this single effect can not be observed in the range of these data under the chosen conditions, the supposed dependency in Fig. 6 results from statistical errors.

The applied mathematical model does not fit the experimental data observed for the catalyst activity because of the unknown deactivation reactions at the catalytic center.

Nevertheless, the experimental results for melting points and molecular masses match well with the mathematical prediction.

4. Conclusions

In respect to the catalyst activity of the system (1)/(3) a cocatalyst/catalyst ratio of three is the optimum, while a certain amount of TIBA has to be added as scavenger to guarantee high activities. After reaching a maximum a further increase of TIBA to the polymerization solution

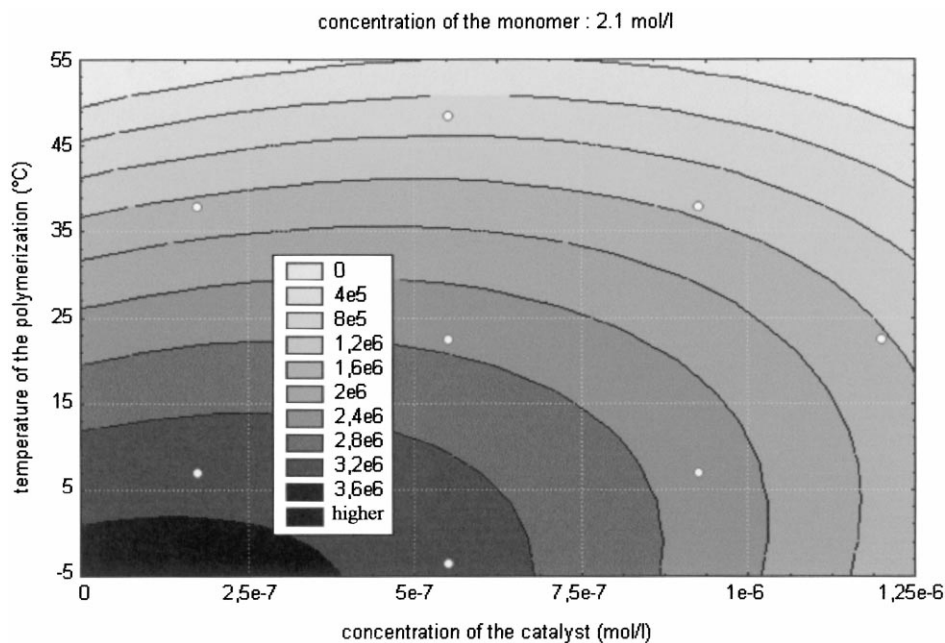


Fig. 5. Surface response plot of the molar mass as a function of concentration of the catalyst and temperature. Conditions: 200 ml of toluene; catalyst conc.,  $1 \times 10^{-7}$ – $1.2 \times 10^{-6}$  mol/l; monomer conc., 1.4–2.8 mol/l; cocatalyst/catalyst ratio, 3; TIBA conc., 0.001 mol/l; temp., –3 to 48.5°C; time of polymerization, 10–60 min.

does not have an effect on either activity nor molar mass. If the system with the borate as cocatalyst is optimized it is a good competitor towards the more commonly used system with MAO.

In the second part of the paper we have shown that a design of experiments can be a promising method to study

interactions between experimental factors in respect to a specific target property.

Under the chosen conditions the mathematical model did not match with the experimental data for the polymerization activities and therefore no statements about dependencies can be found.

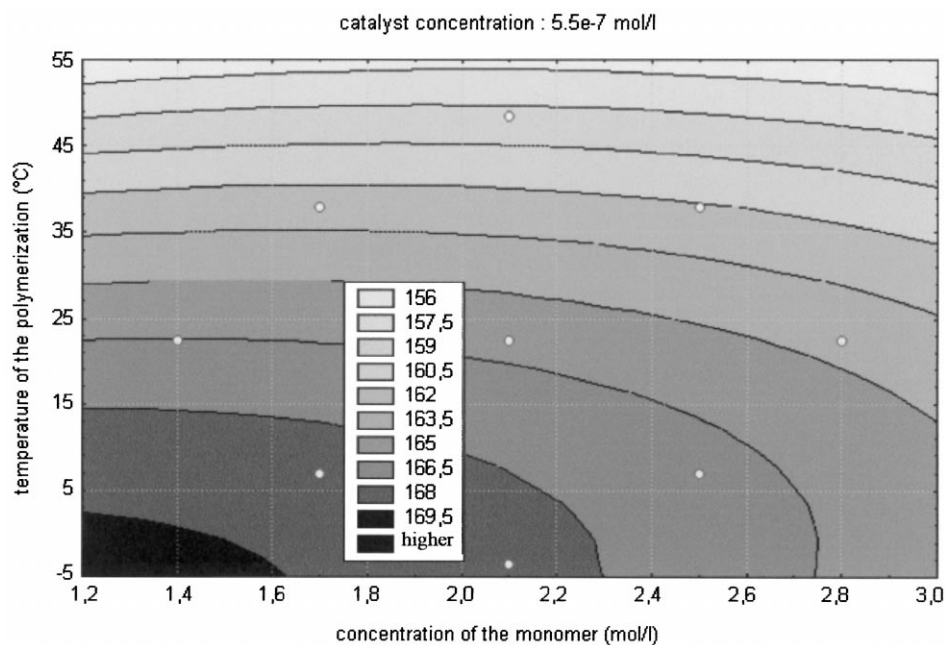


Fig. 6. Surface response plot of the melting point as a function of the concentration of the catalyst and the monomer. Conditions: 200 ml of toluene; catalyst conc.,  $1 \times 10^{-7}$ – $1.2 \times 10^{-6}$  mol/l; monomer conc., 1.4–2.8 mol/l; cocatalyst/catalyst ratio, 3; TIBA conc., 0.001 mol/l; temp., –3 to 48.5°C; time of polymerization, 10–60 min.

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