

# Copolymerization of Ethylene/5-Ethylidene-2-Norbornene with Bis (2-phenylindenyl) Zirconium Dichloride Catalyst: I. Optimization of the Operating Conditions by Response Surface Methodology

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**ABSTRACT:** In this study, the copolymerization of ethylene with nonconjugated diene (5-ethylidene-2-norbornene) was carried out with a bis(2-PhInd) ZrCl<sub>2</sub> metallocene catalyst. Some polymerization factors that were considered affective on the catalyst activity, including comonomer content in the feed, ethylene pressure, and polymerization temperature, were investigated via response surface methodology to determine the optimum polymerization conditions. We found that the comonomer content in the feedstock had no enormous effect on the catalyst activity depression. Also, the polymerization temperature increment through the scrutinized range decreased the copolymerization activity. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

**KEYWORDS:** functionalization of polymers; polyolefins; catalysts; copolymers

Received 31 October 2012; accepted 28 December 2012; published online

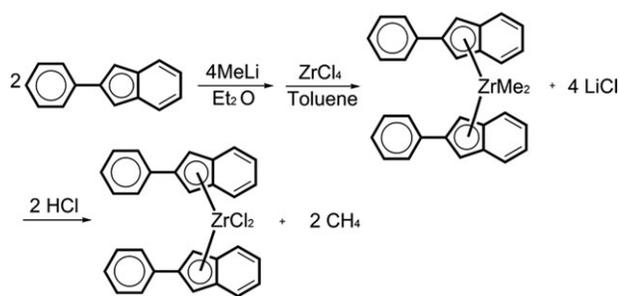
**DOI:** 10.1002/app.38972

## INTRODUCTION

Olefin functionalization is one of the most important areas of polymer science and has garnered much attention these days. A facile route to functionalize olefins is the copolymerization of ethylene with a monomer bearing substituents with latent reactivity as  $\alpha$ - $\omega$  dienes, which are less harmful for the catalyst. Therefore, catalysts exhibiting remarkable activities with better comonomer incorporations are potentially important. In a movement toward this goal, metallocenes offer several advantages over both traditional Ziegler–Natta and late-transition-metal catalysts. In the former, the rate of copolymerization of olefins with polar monomers is low because of the poisoning of the active centers via polar functionalities due to its high oxophilic nature. Also, its polar monomer incorporation rate into the polymer chain is low. On the other hand, late-transition-metal catalysts show a higher tolerance to polar groups, but they still suffer from lower polymerization activities in comparison with metallocenes.<sup>1–4</sup> Consequently, a high catalytic activity and comonomer incorporation and a narrow molecular weight and compositional distribution have caused them to be considered as a promising type of olefin copolymerization catalysts.<sup>5–8</sup> In recent studies, it has been illustrated that among different types of metallocene catalysts, nonbridged half titanocenes<sup>9,10</sup> and substituted metallocenes<sup>5,11</sup> are efficient catalysts with high activity and comonomer incorporation. In addition, a series of single-site catalysts have been reported for the production of new polyolefin materials with well-defined architectures.<sup>12–15</sup>

Cyclic olefin copolymers are a new class of olefin copolymers with significant properties that can be customized through variation of the chemical structure of the copolymer. Their noticeable transparency, low birefringence, extremely low water absorption, excellent water-vapor-barrier properties, excellent biocompatibility, good resistance to acid and alkalis, and their high rigidity makes them desirable materials for optical applications, such as lenses, sensors, and compact disc players, the primary packaging of pharmaceuticals, food packaging, standup pouches, and others.<sup>16–21</sup> The synthesis of cyclic olefin copolymers, especially ethylene–norbornene copolymer, has been studied in detail by several groups.<sup>10,20,22–24</sup> Particularly through the use of cycloolefins such as 1,5-cyclooctadiene, 2,5-norbornadiene, 5-vinyl-2-norbornene, dicyclopentadiene, and 4-vinyl-1-cyclohexene as comonomers, an important class of copolymers can be produced with unsaturated cyclic units in their main chain. The unsaturated group can be efficiently converted to different functional groups to enhance polyolefin's properties.<sup>25–27</sup>

Because the chemical structure of the copolymer is influenced by the polymerization operating conditions, the production of a high-quality polymer requires optimal operation of the reactor. To determine the optimum polymerization conditions and the effects of the operation factors on the polymerization responses, the use of response surface methodology (RSM) is an efficient solution.<sup>28,29</sup> Traditionally, it was common to detect the changes that occur in response to each operation factor separately, that



Scheme 1. Catalyst synthesis.

is, by the full factorial method. In this case, each of the other factors were maintained at constant values during the examination. It is clear that one of the disadvantages of this method was the great number of experiments and the subsequently high cost, time, and material consumption. Nowadays, the use of statistical methods for experiment design can act as a panacea. RSM is a suitable statistical method in which develops regression equations on the basis of mathematical and statistical methods, to make a correlation between parameters and responses.

In this work, the kinetic behavior and performance of the metallocene catalyst bis(2-PhInd)ZrCl<sub>2</sub> in the copolymerization of ethylene with 5-ethylidene-2-norbornene (ENB) was verified, and the operating copolymerization factors were investigated via RSM to determine the optimum operating conditions. The data were analyzed through (Minitab Inc., State College, Pennsylvania) 16 software, and the optimum operating conditions were determined for the maximum catalyst activity.

## EXPERIMENTAL

### Materials

All manipulations involving air- and/or moisture-sensitive compounds were performed in an atmosphere of high-purity argon with Schlenk or glovebox techniques. Methyl aluminoxane (a 10 wt % solution in toluene) and ENB were purchased from Aldrich Chemical Co. (Munich, Germany). Toluene and polymerization-grade ethylene were obtained from Bandar Emam Petrochemical Co. (Bandar Mahshahr, Iran). Toluene was boiled over sodium and distilled. ENB was purified by reduced-pressure distillation at 70°C after it was dried over calcium hydride for several days. Both toluene and ENB were kept over 4-Å/13× activated molecular sieves before use.

### Preparation of the Catalyst

The bis(2-PhInd)ZrCl<sub>2</sub> (Scheme 1) was synthesized with an indirect method.<sup>30</sup> First, MeLi (20 mmol) was added to 2-phenylindene (10 mmol) dissolved in Et<sub>2</sub>O (30 mL) over a period of about 5 min at room temperature. Then, the mixture was stirred for 40 min after the addition of ZrCl<sub>4</sub> (5 mmol) dispersed in toluene (30 mL) added at once. Afterward, the suspension was stirred for 90 min at room temperature. Then, the product was filtered, treated at room temperature with HCl (10 mmol), and stirred for 60 min. The final turmeric color product was obtained by the removal of the solvent under reduced pressure.

Table I. Box–Behnken Design of the Experiments and the Polymerization Results

Run	Factor 1: <i>P</i> (atm)	Factor 2: <i>T</i> (°C)	Factor 3: Comonomer (mmol)	Response: Activity (×10 <sup>2</sup> kg mol <sup>-1</sup> h <sup>-1</sup> )
1	2	30	40	0.91
2	6	30	40	7.62
3	2	70	40	0.32
4	6	70	40	4.81
5	2	50	20	0.27
6	6	50	20	5.67
7	2	50	60	0.06
8	6	50	60	5.54
9	4	30	20	4.27
10	4	70	20	1.41
11	4	30	60	2.18
12	4	70	60	1.97
13	4	50	40	3.10
14	4	50	40	2.97
15	4	50	40	2.99

Conditions: [Al]/[Zr] = 680:1, toluene = 100 mL, catalyst amount = 4 × 10<sup>-6</sup> mol of Zr, and polymerization time = 30 min.

Yield = 3.65 gr (67%). <sup>1</sup>H-NMR (δ): 7.59 (d, 4H), 7.39 (m, 4H), 7.27 (m, 2H), 7.19 (dd, 4H), 7.02 (dd, 4H), 6.55 (s, 4H).

### Experimental Design

RSM was used to design experiments to investigate the effect of the operating factors on the catalyst activity as a polymerization response and to determine the optimum operating conditions. According to our previous studies,<sup>8</sup> the comonomer content in the feedstock, ethylene pressure, and polymerization temperature were considered as the operating factors that affect the catalyst activity in copolymerization, and with RSM, the validity of this consideration was verified. To design the experiments, we used a three-level, three-variable Box–Behnken design, so the comonomer contents in the feed, ethylene pressures, and polymerization temperature levels were specified at 20, 40, and 60 mmol of ENB; 2, 4, and 6 bar of ethylene; and 30, 50, and 70°C, respectively. The designed experiments are shown in Table I.

### Copolymerization

Ethylene copolymerization was carried out in a 200-mL, high-pressure stainless steel reactor that was purged by heating to 90°C while highly pure argon was passed through it for 45 min. Afterward, the reactor was cooled to 25°C, and toluene was introduced into it and saturated with ethylene (1.2 bar). Then, methyl aluminoxane was injected, and a sufficient amount of comonomer was added. Ten minutes later, the specified amount of catalyst was introduced, and the reactor temperature and pressure were increased to the desired values. Then, we started the reaction by turning on the magnetic stirrer. At the end of polymerization (30 min), the reactor content was poured into

**Table II.** Catalytic Behavior and Physical Properties of the Ethylene/ENB Copolymers

ENB in the feed (mmol)	Comonomer in the feed (%)	Activity ( $\times 10^3$ kg mol <sup>-1</sup> h <sup>-1</sup> )	$T_m$ (°C)	$X_c$ (%)	Comonomer in the copolymer (%)	Conversion of the comonomer (%)	Density (g/cm <sup>3</sup> )	CEF
0	0	1.81	140.7	67.1	0	-	0.955	1.00
20	3.7	1.72	108.7	16.9	2.27	61.35	nd	0.95
40	12.5	1.45	91.4	7.7	6.28	50.24	1.069	0.80
80	18.6	1.13	74.3	3	9.10	48.92	1.090	0.63

nd, not determined.  $X_c$ : polymer crystallinity. Conditions: temperature = 70°C, monomer pressure = 6 atm,  $[Al]/[Zr]$  = 545:1, toluene = 150 mL, polymerization time = 30 min, catalyst amount =  $1 \times 10^{-5}$  mol of Zr.

an excess of methanol, filtered, and dried overnight at room temperature.

### Polymer Characterization

All of the differential scanning calorimetry results were obtained with a (Mettler-Toledo Inc., Columbus, Ohio) instrument (model 823<sup>c</sup>) interfaced to a digital computer equipped with Star E 9.01 software (Sencor FRS5). Because the previous thermal history of a polymer affects the measured melting point and degree of crystallinity, the samples are evaluated after they were subjected to a common thermal treatment; this consisted of heating the samples to 160°C at 10°C/min and cooling them to 25°C at -10°C/min. Therefore, the melting point and crystallinity were determined according to the results obtained.<sup>1,31</sup> The density of the polymer was calculated with an Ohuas Voyager Pro VP64C balance with a densitometer. The comonomer presence in the copolymer chains was proven with NMR, and its content was calculated through the NMR results.

## RESULTS AND DISCUSSION

Table II shows the copolymer properties and copolymerization behavior of ethylene/ENB. We found that when we increased the comonomer content in the feed, the melting temperature ( $T_m$ ) and crystallinity of the copolymer decreased. In addition, higher concentrations of the comonomer increased the possibility of its incorporation into the polymer chain, and consequently, because of the addition of branches,  $T_m$  and the crystallinity of the copolymer decreased, and the glass-transition temperature increased.<sup>8,30,32,33</sup>

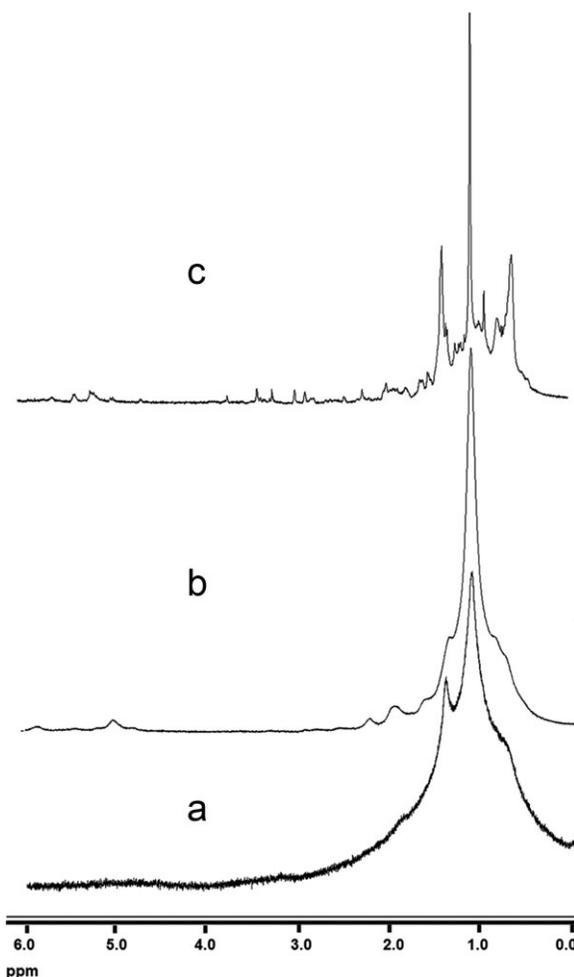
The *comonomer effect factor* (CEF) is defined as the ratio of average copolymerization to homopolymerization and is usually used in investigations of copolymerization behavior.<sup>8</sup> The observed results of  $CEF < 1$  indicated that a rate depression effect occurred in this homogeneous catalytic system. The negative trend observed for CEF in copolymerization was attributed to a competitive coordination of the comonomer to the active center; this resulted in a possible deactivation of some catalytic centers. Although different behaviors were observed in different catalytic systems, this rate depression was attributed mainly to the use of bulky comonomers.<sup>34</sup>

The density study of the copolymers showed that with increasing cyclic content in backbone of the copolymer, the density of

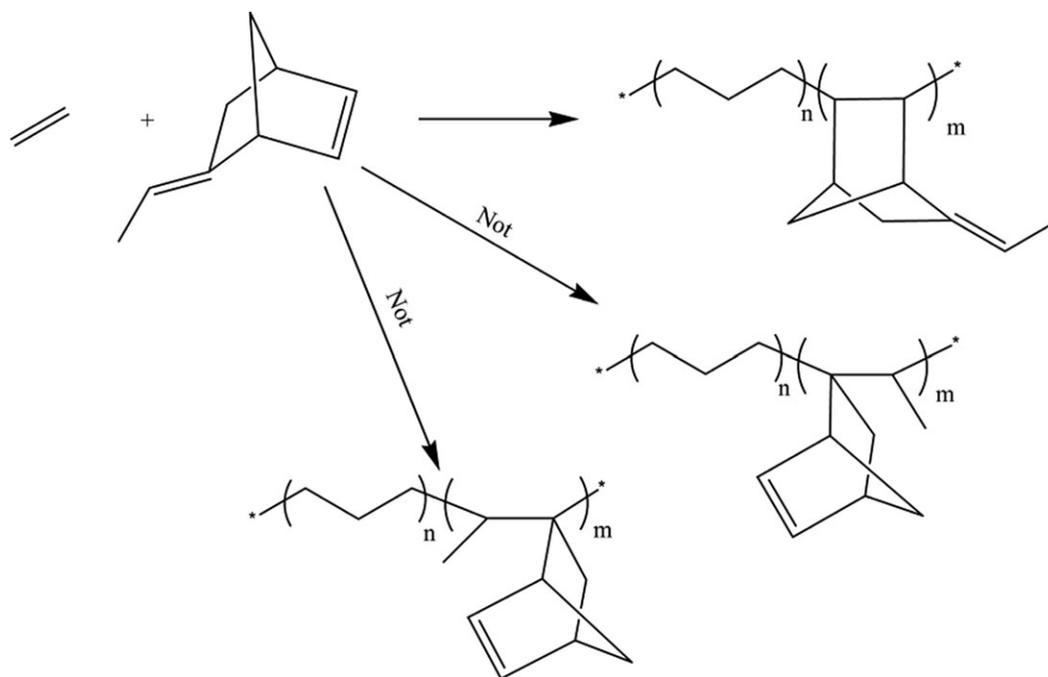
the polymer increased in such a way that it reached values higher than 1.00 (g/cm<sup>3</sup>), which is one of the specifications of these kinds of copolymers.<sup>4</sup>

According to the <sup>1</sup>H-NMR spectra shown in Figure 1, the ENB content was calculated on the basis of Eq. (1):<sup>18,35</sup>

$$\text{ENB(mol\%)} = (A / \{ [0.25 \times (B - 11A)] + A \}) \times 100 \quad (1)$$



**Figure 1.** <sup>1</sup>H-NMR spectra of the ethylene/ENB copolymer: (a) 20, (b) 40, and (c) 80 mmol of ENB.



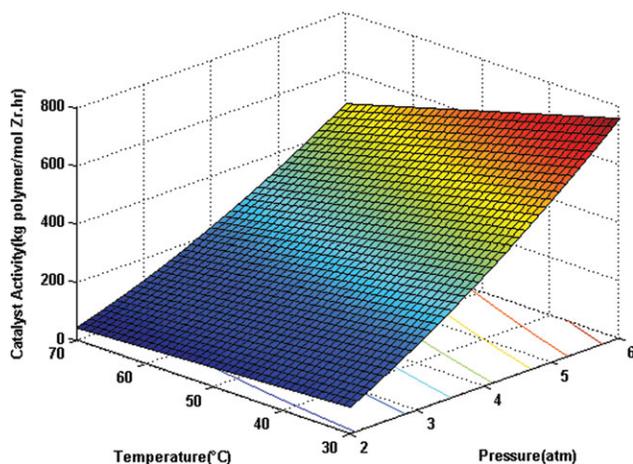
**Scheme 2.** Stereoregularity of ethylene/5-ethylidene-2-norbornene copolymer.

where  $A$  is the integral of the ethylidene hydrogen signals in the range from 4.8 to 5.3 ppm and  $B$  is the integral over all of the other hydrogen signals from 0.5 to 3.0 ppm.

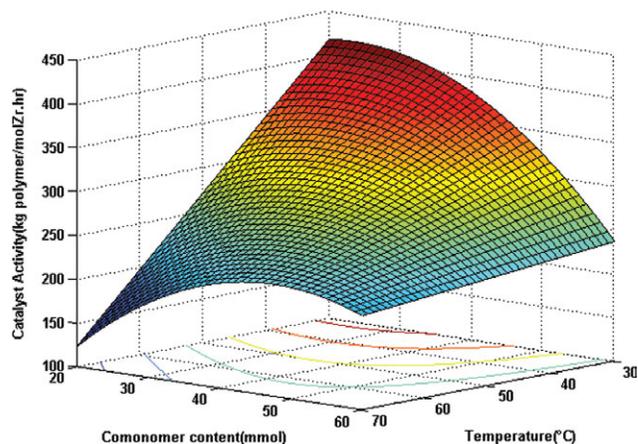
It was clear that with increasing ENB concentration in the feed, the content of ENB in the copolymer increased. Furthermore, the absence of an endocyclic double-bond signal at 5.8–6.0 ppm and the presence of an ethylidene portion between 4.8 and 5.3 ppm in the spectra of the ethylene/ENB copolymers indicated that ENB was copolymerized regioselectively through the endocyclic double bond, whereas the ethylidene group remained intact, perhaps because of the ring strain of the endocyclic double bond (Scheme 2).<sup>18,36</sup>

To locate the optimal copolymerization conditions for maximum catalyst activity, several experiments were designed via the Box–Behnken method. The polymerization results are listed in Table I.

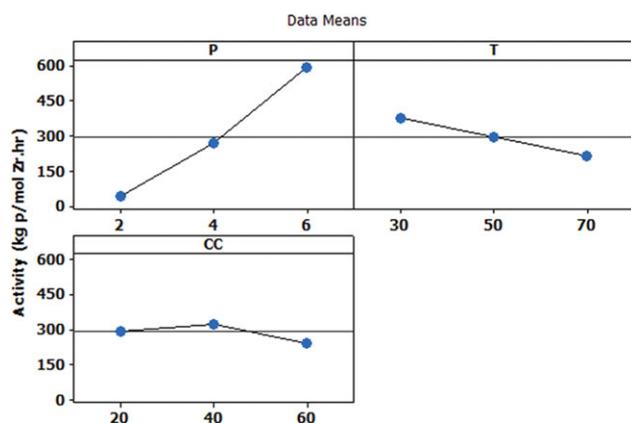
The effects of the ethylene pressure and polymerization temperature on the catalyst activity are shown in Figure 2. The results show that the ethylene pressure was a more effective factor on the catalyst activity than the polymerization temperature. Indeed, the increase in ethylene pressure resulted in an increase in its solubility in the polymerization media and consequently raised its concentration near the active center.



**Figure 2.** Catalyst activity as a function of the temperature ( $^{\circ}\text{C}$ ) and ethylene pressure (atm). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3.** Catalyst activity as a function of the comonomer content in the feed (mmol) and the polymerization temperature ( $^{\circ}\text{C}$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

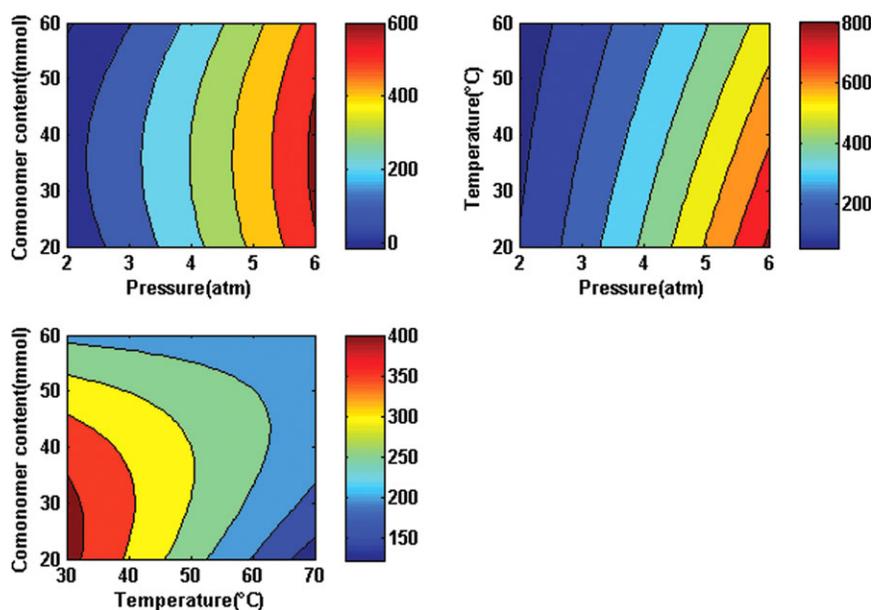


**Figure 4.** Main effects of the operating factors on the catalyst activity. (P: ethylene pressure, T: polymerization temperature, CC: comonomer content) [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

As illustrated in Figure 3, a decrease in the polymerization temperature gave rise to the catalyst activity, and an increase in the comonomer content at lower temperatures reduced it. This was attributed to the lower ethylene solubility in the polymerization media with increasing temperature.

The effect of each factor on the catalyst activity is shown in Figure 4. As shown, ethylene pressure was the most effective factor determining the catalyst activity.

In Figure 5, the contour plots of the effects of different operating parameters on the catalyst activity are shown. According to these plots, the limits of the optimum polymerization conditions for the greatest activity of the catalyst were defined, and with a response optimizer, the optimum point was found at an ethylene pressure of 6 atm, a polymerization temperature of 30°C, and a comonomer content in the feed of 23 mmol.



**Figure 5.** Contour plots of the catalyst activity. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

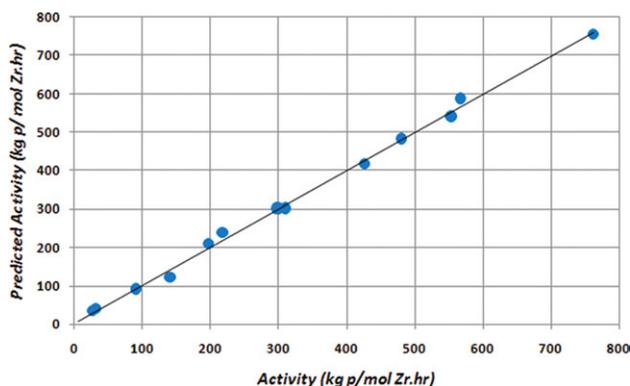
**Table III.** ANOVA Table

Source	$F_{\text{value}}$	$P_{\text{value}}$
Regression	333.66	<0.000
Linear	725.53	<0.000
$P$ (atm)	1991.58	<0.000
$T$ (°C)	170.80	<0.007
Comonomer (mmol)	14.21	<0.000
Square	30.53	<0.000
$P$ (atm) $\times$ $P$ (atm)	20.67	<0.003
Comonomer (mmol) $\times$ Comonomer (mmol)	36.18	<0.001
Interaction	48.98	<0.000
$P$ (atm) $\times$ $T$ (°C)	40.39	<0.000
$T$ (°C) $\times$ Comonomer (mmol)	57.57	<0.000
Lack of fit	7.87	0.117

According to the system response variation with the operating factors, Eq. (2) was obtained:

$$\begin{aligned} \text{Activity} = & -1.7 + 125P - 5.12T + 146 \text{ Comonomer} + 10.3P^2 \\ & - 0.137 \text{ Comonomer}^2 - 1.39PT + 0.166T \\ & \times \text{Comonomer} \end{aligned} \quad (2)$$

where  $P$  is the pressure and  $T$  is the temperature. To fit a proper model, parameters in which the  $P$  value was more than 0.05 were omitted. In Table III, the analyses of variance (ANOVAs) show that the model coincided well with the actual results. The  $F$  value of the model was 314.71; this implied the validity of the model.



**Figure 6.** Actual activities of the catalyst versus corresponding predicted ones. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Finally, the actual activities versus the predicted ones are plotted in Figure 6. The deviation from the  $x = y$  line show the differences between the predicted amounts of activity and their corresponding actual ones. The less the deviation from the line is, the greater the accuracy of a model in the defined operating conditions region is. The results show that the predicted model was in good agreement with the actual amounts of the activity, with a regression coefficient ( $R^2$ ) of 99.68%.

## CONCLUSIONS

The copolymerization of ethylene with ENB was investigated.

The bis(2-PhInd)ZrCl<sub>2</sub> showed good ENB incorporation in the copolymerization. Also, we observed that when we increased the comonomer feed ratio, the comonomer content in the backbone of the polymer increased. The CEF values of less than 1 for the ethylene/ENB copolymerization showed that the rate depression behavior was dominant. The densities of the ethylene/ENB copolymers increased with increasing ENB content and reached values higher than one.

The Box–Bekken design method was used to define experiments to investigate the effects of different operating factors. We found that the ethylene pressure was the most effective factor on the catalyst activity, and when it was increased, the activity of the catalyst increased. The optimum region and point for the polymerization were found via the contour plots and response optimizer of the software at an ethylene pressure of 6 atm, a polymerization temperature of 30°C, and a comonomer content of 23 mmol. Finally, a model was fitted to the obtained catalyst activities, and its accuracy was checked by ANOVA, plotting of the actual activities versus the predicted ones, and calculation of the  $r^2$  of the resultant plot. The  $r^2$  was 99.68 in this case, which indicated good agreement of the predicted amounts of the activity with the corresponding actual ones and the accuracy of the model.

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