Study of Ziegler-Natta/(2-PhInd)$_2$ZrCl$_2$ hybrid catalysts performance in slurry propylene polymerization

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ABSTRACT

Several types of hybrid catalysts are made through mixing of 4th generation Ziegler-Natta (ZN) and (2-PhInd)$_2$ZrCl$_2$ metallocene catalysts using triethylaluminum (TEA) as coupling agent. Response surface methodology (RSM) is used to evaluate the interactive effects of different parameters including amounts of metallocene and TEA and temperature on metallocene loading. Analyzing the amounts of Al and Zr elements in the hybrid catalysts through ICP-OES and EDXA reveals that temperature plays a crucial role on anchoring of the metallocene catalyst on ZN while TEA has the least determining effect. The ICP analysis shows that as the concentration of Al goes up in the hybrid catalyst the concentration of Zr passes a maximum, while EDXA shows a direct relationship between the Al and Zr contents. Using triisobutylaluminum (TIBA) and methylaluminoxane (MAO) as the coupling agents, almost similar metallocene loadings are observed. Finally, the performance of hybrid catalysts is investigated in propylene polymerization and the obtained polymers are characterized using DSC and DMTA through which the presence of two types of polymers in the final product are confirmed. **Polyolefins J (2015) 2: 73-87**

Keywords: Hybrid catalysts; Ziegler-Natta; metallocene; surface analysis; bulk analysis; polypropylene

INTRODUCTION

on the way of producing polyolefins with novel characteristics, researchers moved toward designing novel polymerization catalysts. Catalyst alloys, hybrid catalysts and multi – catalyst systems can be considered as the smartest approaches toward this goal [1-5]. In these systems each catalyst produces polymers with unique characteristics and therefore final polymer is a blend of two or more kinds of polymers.

So far some strategies have been developed for making polymeric reactor alloys. For example, in one of the strategies, a series of reactors (tandem or cascade reactor systems) is used and each reactor runs under different polymerization reaction conditions, generating the desired bimodal polymers with different molecular weights and microstructures [6]. In another strategy, polymer structures are changed by changing operation conditions and hydrogen pressure in a single reactor during polymerization. Otherwise, an alternative way is implemented by combining different catalysts to form multi-catalyst or hybrid systems in which each active site produces a polymer with unique characteristics when polymerization conditions are met [7-9]. Another rapidly developing approach, which

has the ability to produce polymeric reactor alloys, is the use of the mixtures of catalysts and preformed polymer particles [10, 11]; in this case the primitive polymer particle act as a reaction bed for another catalyst. One more method is by changing the feed of the reactor that is used in conventional reactor granule technology (RGT) in which one type of catalyst is responsible for producing different types of polymers usually polypropylene and ethylene-propylene rubber [12, 13].

Up to now various types of hybrid catalysts including Ziegler-Natta/metallocene [1-6, 14-17], metallocene/metallocene [18-25], metallocene/late TM [26- 31], and finally. Late TM/Late TM [32] have been studied in polymerizing different types of monomers and comonomers for producing polymeric reactor alloys. Among the aforementioned hybrid catalysts, Ziegler-Natta/metallocene hybrid catalysts have been widely studied and usually it is anticipated that the final hybrid catalyst can combine the advantages of ZN catalyst in morphological control and metallocene catalyst in polymer chain microstructure control [5]. Different methods may be used for making these types of catalysts. One method is through the use of a third component like aluminum alkyls (AlR_3) whether through mixing all the components with each other at the same time [5] or pretreating metallocene catalyst with AlR_3 and then reacting with ZN component [8, 9]. Other methods include simple physical mixing of the two catalysts at specific temperatures [7], or loading two kinds of catalysts on a same support (e.g. $MgCl_2$. nROH adduct) [7].

The effect of reaction parameters on final hybrid catalyst can be analyzed individually; but experimental design helps verify whether or not there is an interactive effect between the reaction parameters. Traditionally, trial and error method has been practiced to investigate the effect of each single parameter. This optimization technique, which is called one-variable-at-a-time, does not include the interactive effects among the variables studied and increases the number of experiments necessary to conduct a research, which leads to an increase in time and expenses [33]. As a solution, the statistical method of response surface methodology (RSM) has been proposed to include the influences of individual factors as well as their interactive influences by fitting of a polynomial equation to the experimental data. In the experimental design there are ''Factors'' or independent variables which are experimental variables that can be changed independently of each other. Each variable has different
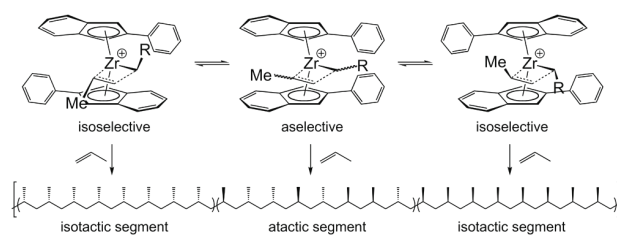
Scheme 1. Believed oscillating mechanism of $(2\text{-PhInd})_2ZrCl_2$ in producing stereoblock elastomeric PP.

''Levels'' at which the experiments must be carried out. In each experimental design, the measured values of the results from experiments are ''Responses'' or dependent variables [33].

In the present paper a novel approach is introduced and used for the preparation of ZN/metallocene hybrid catalysts. The ZN part is of the famous 4th generation type and the metallocene part is $(2\text{-PhInd})_2ZrCl_2$ which is famous for producing stereoblock elastomeric PP due to its so-called oscillating performance in polymerization (Scheme 1) [34-36]. The preparation method consists of two stages. At first the ZN component is reacted with TEA and after complete washing and drying at 60ºC the resulted product is reacted with the metallocene component at different mixing temperatures. To investigate the effect of different parameters on the loading amount of metallocene a series of experiments is designed using Design Expert 6.0 response surface methodology. In these experiments the effects of TEA concentration, metallocene concentration and temperature are fully studied on the amount of loaded metallocene. Finally, two other types of hybrid catalysts are also made in which MAO and TIBA are used as the coupling agents and in the TEA case the best reaction conditions found in experimental design are used for making them. At last, polymerization of propylene is investigated using the hybrid catalysts and the resultant polymers are analyzed by DMTA and DSC analyses.

EXPERIMENTAL

Materials

2-Phenyl Indene and methylaluminoxane (MAO; 10 wt% solution in toluene) were obtained from Aldrich chemical Co. (Munich, Germany). Methyl lithium and TIBA were purchased from Merck Chemical Company (Germany). Ethereal hydrochloric acid (2 N) was purchased from Acros Chemical Company (USA). Toluene was provided by Bandar Imam Petrochemical Company (BIPC, Iran) which was refluxed and distilled over sodium before use and kept

over 4A/13X activated molecular sieves. TEA, 4th generation ZN catalyst and propylene were obtained from Maroon Petrochemical Company (Iran). All the manipulations involving air- and/or water-sensitive compounds were performed under an atmosphere of dried nitrogen in a glove box.

Catalyst preparation

Metallocene catalyst

(2-PhInd)$_2$ZrCl$_2$ was synthesized using a modified version of the literature method [37-40]. The final product was obtained by removing the solvent under reduced pressure. A fine yellow powder was obtained and characterized by ^{1}H NMR (solvent: CDCl$_3$): 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).

Hybrid catalyst

To find an appropriate method for making hybrid catalysts some preliminary investigations were done. Three different methods were examined at first, including: simple mixing of ZN and metallocene catalysts at different temperatures; adding the catalysts and alkyl aluminums in separate stages and different temperatures; and adding all the components in a single step at different temperatures. Afterward, the resultant hybrid catalysts were studied by EDXA and the method, that led to the maximum loading of metallocene catalyst on the ZN component, was chosen for further study. As it will be seen later, our studies showed the second method to be more appropriate and therefore the main hybrid catalysts were synthesized in a stepwise manner as follows: specific amounts of TEA were added dropwise to 1 gram of the 4th generation Ziegler-Natta Catalyst (dispersed in 10 ml toluene) at room temperature along with mechanical stirring. After 30 minutes the reaction mixture was washed with dry toluene five times, each time with 20 ml (the filtered liquid became completely colorless). Then the mixture was again washed with 20 ml toluene at 60ºC and finally the solid powder was dried at the same temperature under the flow of dry argon gas. Specific amounts of the metallocene catalyst (2-PhInd)$_2$ZrCl$_2$ (in toluene) were added to the pretreated Ziegler-Natta catalyst at specific temperatures along with mechanical stirring (300 rpm). After 6 hours, the reaction mixture was fully filtered and washed several times with toluene until the filtered liquid became colorless. Two other hybrid catalysts were also synthesized but TIBA and

MAO were used instead of TEA and the reaction conditions were chosen like the ones which resulted in the highest loading of Zr in the TEA case.

Design of Experiments

To thoroughly understand the effect of each parameter (temperature, metallocene and coupling agent) on the ZN/metallocene hybrid catalysts preparation, 17 runs were carried out and a surface response (Box-Behnken) design including the independent variables of temperature (T), triethylaluminum (TEA) concentration and metallocene catalyst concentration was implied. Each factor was varied over 3 levels. The concentration of each element including Al and Zr were considered as the responses. The levels of the independent variables (Table 1) were chosen according to the literature [5, 8, 9]. Also some limitations like availability and cost of materials were considered.

The experimental design proposed by the software along with analysis results are summarized in Table 2.

Polymerization

Polymerization reactions were performed in a 1 liter Büchi reactor (Büchi Glass Uster bmd300) equipped with controlling systems for temperature, stirring speed, and reaction pressure. 500 mL of dried toluene were injected into the reactor. The desired amount of MAO was introduced. The amounts were prescribed such that the molar ratio Al$_{MAO}$/Zr = 500. A measured amount of catalyst (hybrid or pure metallocene) was injected (dispersed in a small volume of toluene) and then the polymerization reaction was conducted at 6 bar of propylene, and 800 rpm for 60 minutes in two steps. In step one, the polymerization was performed at 35ºC for 15 minutes then the temperature was increased to 70ºC and the polymerization was continued for 45 minutes in this temperature. For better control of reaction temperature and rapid change of the temperature from 35ºC to 70ºC, two oil circulators were used. One of them was set at 35ºC and the other at 70ºC. When the first step was finished the oil flow path was changed rapidly through special valves; by this method after five minutes the temperature of the reaction was changed from 35ºC to

Table 1. The levels of independent variables chosen for the study.

Name	Units	Low	High
metallocene Catalyst	g	0.02	0.1
Coupling Agent (TEA)	mmol	5	25
Mixing Temperature	ºC	25	60

Table 2. Experimental Box–Behnken design runs and corresponding results (the responses).

Std	Run	Met (g)	TEA (mL) (1M)	Temp (ºC)	Response 1 Al Wt%	Response 2 Zr Wt %
5	1	0.02	15.00	25.00	2.11	0.21
10	2	0.06	25.00	25.00	2.21	0.18
7	3	0.02	15.00	60.00	2.41	0.25
8	4	0.10	15.00	60.00	1.93	1.12
11	5	0.06	5.00	60.00	2.03	0.64
13	6	0.06	15.00	42.50	2.26	0.59
9	7	0.06	5.00	25.00	2.27	0.49
2	8	0.10	5.00	42.50	2.05	0.96
12	9	0.06	25.00	60.00	2.1	0.7
15	10	0.06	15.00	42.50	2.26	0.59
16	11	0.06	15.00	42.50	2.31	0.62
14	12	0.06	15.00	42.50	2.26	0.67
4	13	0.10	25.00	42.50	2.13	0.23
1	14	0.02	5.00	42.50	2.03	0.33
6	15	0.10	15.00	25.00	2.26	0.25
17	16	0.06	15.00	42.50	2.34	0.54
3	17	0.02	25.00	42.50	2.44	0.18

70ºC. During the temperature change there was a rapid increase in the reaction pressure; therefore to keep the pressure constant, one of the vents of the reactor was kept open until the temperature was reached to 70ºC. The obtained polymers were poured into acidified methanol, collected by filtration, dried, and weighed.

Characterization

EDXA of the preliminary synthesized hybrid catalysts was performed using a VEGA EMITECH K450X instrument at 20kV accelerating voltage after being coated with gold (thickness:15nm, density 19 g cm-3). To achieve the bulk concentration of Al and Zr elements in each hybrid catalyst, they were analyzed by ICP-OES characterization technique using an ICAP 6000 instrument after complete digestion of the samples in acid. The morphology of the hybrid catalysts was investigated through optical microscopy using a JENAVERT microscope coupled with a JVC TK-C1381 Color Video Camera. ^{1}H NMR analysis of the catalysts was performed using a 400 MHz, AVANCE 400 BRUKER NMR Instrument. $CDCl_3$ (for the metallocene catalyst dissolved in toluene) and DMSO-d6 (for ZN and the hybrid catalysts dissolved in methanol) were used as the internal references. DIBP content of each of the catalyst was determined through ^{1}H-NMR analysis. Exact amounts of samples (50 mg) were fully digested in methanol (0.7 ml) [41] and an exact amount of DMSO was added to them; the integral of DMSO was chosen as the comparison base. Specific surface areas of the catalyst were determined

through BET method using a CHEMBET 3000 Quantachrome TPRWin Instrument. FTIR analyses of the catalyst samples were recorded using a FTIR Bruker 55 instrument (Model EQUINOX); for this purpose the samples were mixed with Nujol in a glove box and then the analyses were run. Polypropylenes were characterized through DSC after fractionation using a NETZSCH DSC 200 F3 Instrument. The heating and cooling rates were the same and equal to 10ºC/min. The intrinsic viscosities were determined in decahydronaphthalene at 135±1ºC using a SOFICA-CINEVISCO viscometer serial V04/1CE. For calculation of M_v, the Mark-Houwink-Sakurada equation was used [42]. The requisite constants α and K were not available for elastomeric polypropylene; hence, the constants for atactic polypropylene were employed (α= 0.77; K = 15.8×10^{-3} ml/g); and the constants for the isotactic polypropylene were considered as α = 0.8; K = 11×10^{-3} ml/g [42]. Some of the heptane soluble parts of the samples were also characterized using ^{13}C NMR analysis after dissolving them in $C_2D_2Cl_4$ at 120ºC.

RESULTS AND DICUSSION

In this part the discussions on catalysts and polymers are presented in two separate sections as follows:

Catalyst

As mentioned in the previous sections, after treatment of Ziegler-Natta catalyst with TEA, the catalyst was completely washed and then the resultant catalyst was reacted with the Zirconocene component. Therefore by this method, we could sure that TEA has a role in loading of the metallocene catalyst; i.e. if both of the components (TEA and metallocene) were added simultaneously then it was difficult to recognize whether the metallocene catalyst or TEA has acted as the coupling agent between ZN and TEA.

However three types of mixing were examined: 1. the three components (ZN, TEA and metallocene) were mixed together in one step; 2. the three components were added step-wise; and 3. just the two catalysts were mixed with each other; finally all of them were compared qualitatively. The amounts of each component were selected as follows: ZN: 1 g, Met: 0.1 g, AlR$_3$: 30 mmol. Figure 1 shows the results of EDXA investigation of the synthesized hybrid catalysts.
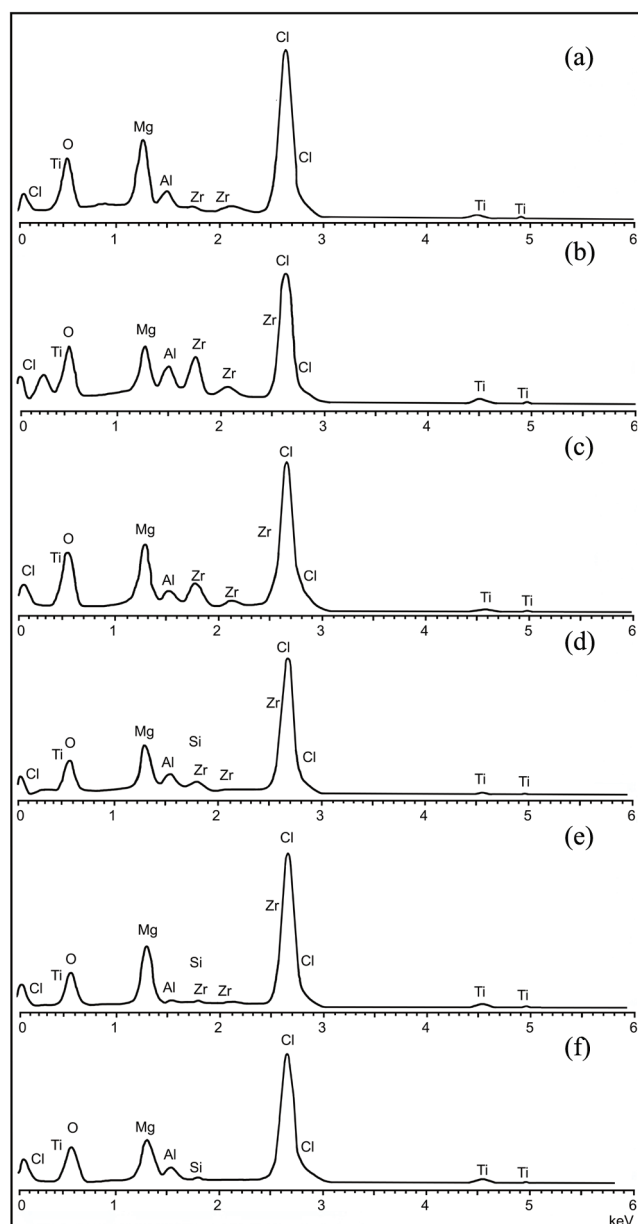
Figure 1. EDXA of catalyst samples: (a) Pure ZN; (b) ZN/Met, 25ºC; (c) ZN/Met,60ºC; (d) (ZN-TEA)/Met, 25ºC; (e) (ZN-TEA)/Met, 60ºC; (f) ZN/TEA/Met, 60ºC. (1 g ZN, 0.1 g Met, Al=30 mmol, mixing time:6h).

Although this method of characterization is rather qualitative than quantitative and its characterization depth is limited to a few micrometers (1µ to 5µ in this case), it can provide some insights into the catalyst composition. From the figure, multiple results can be derived. The first result is that, temperature alone is a determining factor in loading of the second catalyst on the first one. In all the cases as the temperature increased from 25ºC to 60ºC the relative intensity of the Zr peak increased.

The second result was that, when the three components were all mixed together at the same time

(Figure 1, case f) the amount of Zirconocene loading was lower than the cases in which the ZN component was first reacted with TEA and then reacted with Zirconocene (Figure 1, cases d, e); this can show that the interactions between the metallocene catalyst and TEA may produce some species that have a lower tendency to load on the ZN component. And finally, the third general result was that, the presence of an aluminum alkyl can increase metallocene loading (Figure 1, cases d to f in comparison with a to c). From these preliminary observations we decided to chose the second approach for making hybrid catalyst—i.e., at first the ZN component was reacted with aluminum alkyl from room temperature to 60ºC and then the resultant product was reacted with the metallocene component at the reaction conditions that were suggested by Design Expert 6.0 software. The suggested design of experiments (DOE) is shown in Table 2. Finally, the hybrid catalysts were characterized through ICP analysis after acid digestion.

The ICP results (responses) are shown in Table 2 and the results obtained from Design expert analysis are shown in Figure 2. As is clear from Figure 2a, temperature played a determining role in the amount of metallocene loading on the ZN catalyst. As temperature increased, the loading of zirconocene on the ZN surface increased too. This can be caused by two factors. The first factor is that, in all the chemical reactions temperature usually enhances the reactions by providing energy needed for the formation or breaking of the chemical bonds; in this case the probable reactions can occur between Cl ligands present in ZN or metallocene with each of metallic centers like Mg, Zr, Ti and Al. The second factor can be the slight expansion of the ZN catalyst structure at higher temperature which can cause the ZN catalyst to host more zirconocene catalyst in itself.

Another result that can be deduced from the figure is that, at each temperature as the coupling agent concentration (TEA) went up, the amount of Zr loading decreased. This finding may be due to two

Table 3. Effect of TEA (AlEt$_3$) on the specific surface area of the catalyst.

mmol (TEA) *	0	10	20	30
Specific Surface Area (m²/g)	260	230	190	170

*0.1 molar solution of TEA in toluene was added dropwise to 1 gram of 4th generation ZN catalyst dispersed in 10 mL toluene along with mild mechanical stirring.

phenomena. First, alkyl aluminum adsorbed on the ZN catalyst surface has blocked the vacant sites that could be host for zirconocenes. This hypothesis is readily rejected by the results obtained by EDXA. As can be seen from Figure 1, it is completely obvious that as the amount of Al increases, the amount of Zr increases too. This finding supports the positive effect of alkyl aluminum in increasing the loading of metallocene catalyst. The second is that, excess alkyl aluminum has blocked the pores of the ZN catalysts. This hypothesis was examined using BET analysis. As is clear from Table 3, by increasing the mmol of $AlEt_3$, the specific surface area of the ZN catalyst came down considerably, decreasing from 260 m^2/g to 170 m^2/g. Therefore it can be concluded that, $AlEt_3$ has acted as a blocking agent for the catalyst. This phenomenon inhibits the penetration of the metallocene component into the pores, cracks, and crevices in the ZN catalyst particles and therefore the amount of Zr loading decreases.

Figure 2b is indicative of two facts. The first fact is

that, by increasing the coupling agent concentration, zirconocene loading came down which its reasons were mentioned before. The second fact is that, by increasing the metallocene concentration in the reaction media the amount of Zr loading went up steadily. This trend seems to be logical according to the fundamental principles of chemistry. As the concentration of zirconocene goes up in the reaction media the probability of reaction, whether chemical or physical, goes up and therefore loading goes up too. From these results one would expect that finally the amount of loading should reach a constant value due to limited reaction sites on the ZN catalyst.

Figures 2c and 2d show changes in the Al contents of the hybrid catalysts. As is clear from Figure 2c, the changes in the Al content of the catalyst are very small as temperature goes up. This can be indicative of the strong chemical bindings occurred between the ZN catalyst and Al. Al has a vacant orbital that can host electron pairs. Considering the very high concentration of Cl in the ZN catalyst, it seems very
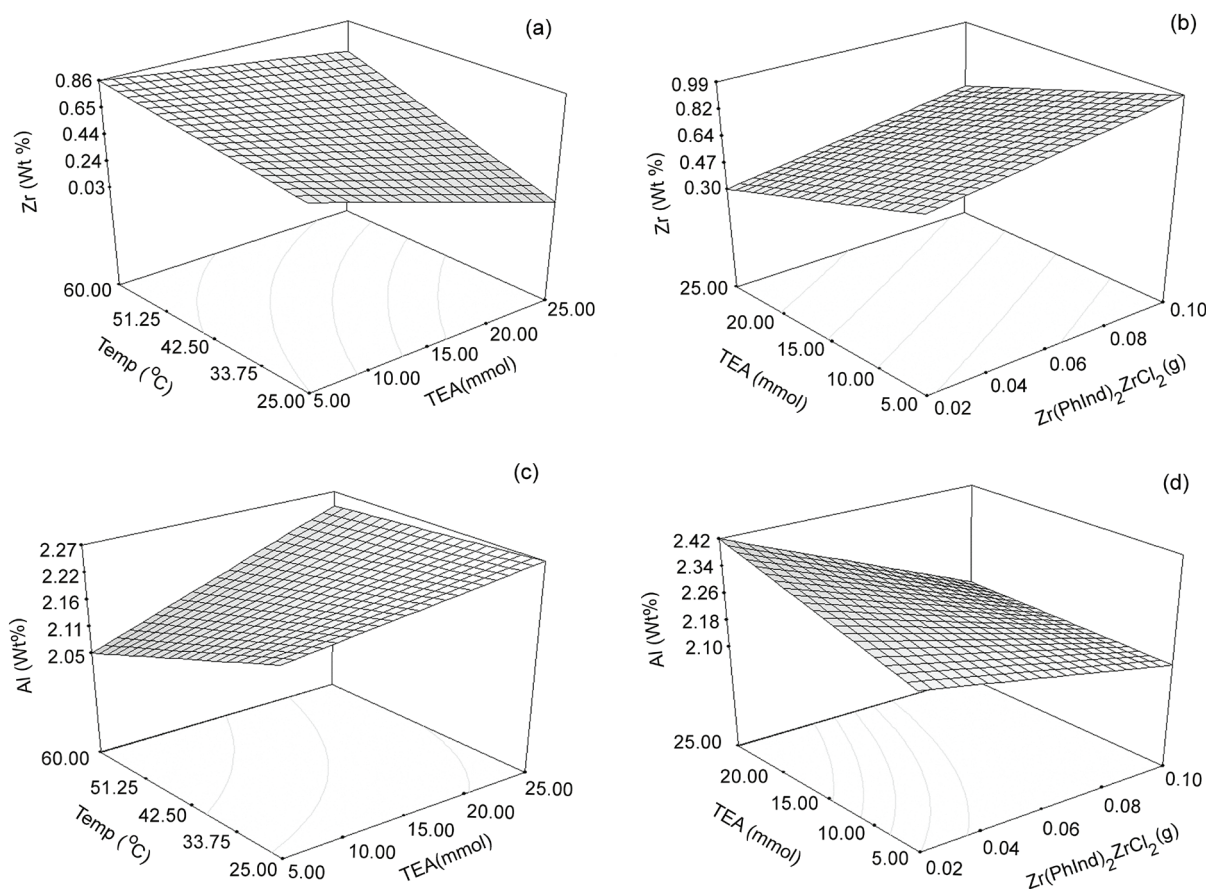

Figure 2. Results obtained from DOE (a), (c): The metallocene conc. is considered as mean value i.e. 0.06 g, (b),(d): Temperature is considered as the mean value that is 42.5°C.

Table 4. Analysis of variance table ANOVA for Response Surface 2FI Model, Response: Zr.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	1.08	6	0.18	11.66	0.0005
A (Met Conc)	0.32	1	0.32	20.50	0.0011
B (AlR$_3$ Conc)	0.16	1	0.16	10.36	0.0092
C (Temp)	0.31	1	0.31	20.25	0.0011
AB	0.084	1	0.084	5.46	0.0416
AC	0.17	1	0.17	11.17	0.0075
BC	0.034	1	0.034	2.22	0.1670
Residual	0.15	10	0.015	10.65	0.0192
Lack of Fit	0.15	6	0.024		
Pure Error	9.08E-003	4	2.270E-003		
Cor Total	1.23	16			

The Model F-value of 11.66 implies the model is significant. There is only a 0.05% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB and AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

probable that Al can host Cl electron pairs and therefore not be removed readily from the ZN catalyst by simply increasing temperature and several washing. Another finding is that, by increasing the TEA concentration the amount of loaded Al also increased. Figure 2d seems to be rather strange. On the first look, it may be concluded that the metallocene catalyst has substituted the aluminum alkyls and therefore the Al loading is come down; but the truth is that since the metallocene catalyst is heavy (M$_w$= 547 gmol^{-1}) therefore when it is being loaded on the ZN component the overall hybrid catalyst becomes heavier and therefore the weight percent of Al comes down. Another finding is that, by increasing the alkyl aluminum concentration the weight percent of Al is gone up.

In the fitting step in DOE the best model that best fitted the obtained results was the 2FI model. In this model, in addition to the main parameters (A: Met Conc, B: AlR$_3$ Conc, C:Temp) their simultaneous effect (AB, AC, BC) are also considered on the results. The analysis of variance for the responses

are shown in Table 4 and Table 5 for the Zr and Al contents, respectively and as is clear from both of the tables the model is completely significant for the results obtained. As is clear from Table 4, A, B, C, AB and AC have the most influenece on the extent of Zr loading. The more the B (AlR$_3$) the less the Zr loading, the more the A(metallocene concentration) and C (temperature) the more the Zr loading and also the more the AC the more the Zr loading. The equation suggested for this case is as follows:

$$Zr = 0.50 + 0.20A - 0.14B + 0.20C - 0.14AB + 0.21AC + 0.09 BC.$$

As is clear from the equation, A, C and AC have the greatest coefficients which means that they are more effective than the other parameters.

From Table 5 for the Al content of the hybrid catalysts, although the AC term is introduced as a significant term but it is meaningless here. The reason for this, is the high M$_w$ of the metallocene component. When the

Table 5. Analysis of variance table ANOVA for Response Surface 2FI Model, Response: Al.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	0.23	6	0.038	3.76	0.0318
A (Met Conc)	0.048	1	0.048	4.76	0.0541
B (AlR$_3$ Conc)	0.031	1	0.031	3.09	0.1090
C (Temp)	0.018	1	0.018	1.79	0.2108
AB	0.027	1	0.027	2.70	0.1316
AC	0.099	1	0.099	9.83	0.0106
BC	4.225E-003	1	4.225E-003	0.42	0.5323
Residual	0.1	10	0.01	11.53	0.0167
Lack of Fit	0.095	6	0.016		
Pure Error	5.520E-003	4	1.380E-004		
Cor Total	0.33	16			

The Model F-value of 3.76 implies the model is significant. There is only a 3.18% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case AC is the only significant model term.

Table 6. Model Summary statistics.

	Std. Dev.	C.V.[a]	PRESS[b]	Adeq. Precision[c]	R²[d]	Adj. R²[e]
Zr	0.12	24.68	0.56	12.99	0.87	0.80
Al	0.10	4.57	0.35	7.83	0.69	0.51

[a] Coefficient of Variance, it shows the reproducibility of the data; values lower than 10% is favorable

[b] Predicted residual error sum of squares;

[c] Adequate precision, measures signal to noise ratio and values higher than 4 is favorable.

[d, e] R squared and Adjusted R Squared.

metallocene is being loaded on the catalyst, the overall weight of the hybrid catalyst goes up considerably and therefore the weight percent of all other consituents of the catalyst comes down. However the equation suggested for Al by the software was as follows:

$$Al = 2.2 - 0.08A + 0.06B - 0.05C - 0.08AB - 0.16AC + 0.03BC$$

As is clear from this equation, parameter B(TEA concentration) showed a positive effect on Al Wt% of the hybrid catalyst and temperature showed a negative effect which could be indicative of this fact that by increasing the temperature some of loosely loaded Al atoms were washed away.

Table 6 shows the model summary statistics. As is clear from the table, the model has an acceptable adequate precision. In the Zr case, the coefficient of variance is rather high, that can be indicative of a lower probability of reproducibility of the results. This can be due to the very high sensitivity of ICP to the weight of each sample. Generally, the reproducibility of ICP results is low.

Finally, in the optimization stage various solutions were suggested by the software to rich maximum metallocene loading (Table 7). By considering different factors especially cost and availability of the reactants, the optimum solution was selected, i.e. the

Table 7. Various solutions suggested by the software to reach the maximum desirability (maximum Zr wt%).

Solutions	Met	TEA	Temperature	Zr wt%	Desirability
1	0.1	8.83	58.24	1.036	1
2	0.1	10.33	57.83	1.031	1
3	0.1	5.40	56.19	1.068	1
4	0.1	9.66	59.17	1.060	1
5	0.09	6.35	58.49	1.021	1
6	0.10	6.40	59.57	1.090	1
7	0.10	11.22	58.79	1.027	1
8	0.10	7.50	59.17	1.070	1
9	**0.10**	**5.10**	**59.49**	**1.090**	**1**
10	0.09	5.16	58.14	1.050	1
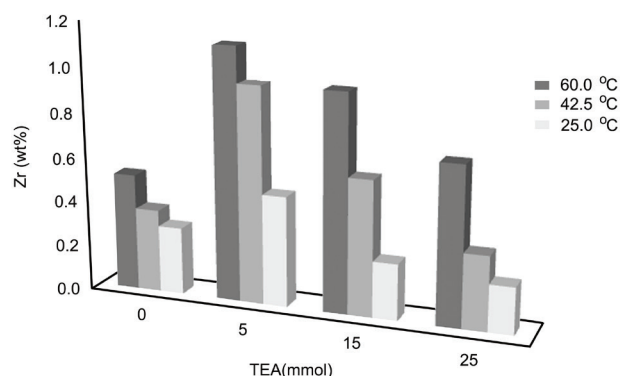
Figure 3. Effect of TEA concentration on amount of Zr loading.

solution number 9 in the table. By using this solution the real Zr content was almost near the predicted value.

For further investigations, the amount of metallocene loading was examined without the presence of coupling agent. As is clear from Figure 3, at first a considerable increase is observed in the Zr content as the Al concentration is increased. After that the concentration of loaded Zr started to decrease as the coupling agent concentration increased. Of course, for most of the cases the amount of loaded Zr was still higher than the amount of the catalyst without coupling agent. By comparing these results with the ones obtained from EDXA, one may see a contradiction in the results at first glance since the ICP analysis (Figure 3) shows that as the concentration of Al, in the hybrid catalyst, goes up the concentration of Zr passes a maximum, while the EDXA result shows a direct relationship between the Al and Zr contents (Figure 1). But as it was mentioned previously, it should be taken into consideration that EDXA is a surface analysis and provides a little information on the bulk of materials while ICP provides complete information on the surface and bulk of materials. According to Figure 1 and Table 3 it can be said that, although aluminum compounds provide surficial sites for the impregnation of metallocene catalyst, they block cracks and crevices of the ZN catalyst and reduces the probability of penetrating the metallocene catalyst in the bulk of ZN catalyst and this is why different

Table 8. The Zr content of hybrid catalysts synthesized with different coupling agents.

Coupling agent	Wt% Zr
TEA	1.2
MAO	1.0
TIBA	0.9

Table 9. DIBP content of the catalysts.

Ziegler- Natta catalysts*	DIBP content
Untreated	100
Treated with TEA (5 mmol)	27
Treated with TEA (25 mmol)	23
Treated with TIBA (5 mmol)	35
Treated with MAO (5 mmol)	18

*0.1 g catalyst treated with 5 and 25 mL co-catalyst (1 molar in toluene).

Table 10. Ti content of the treated catalyst.

Catalysts *	Ti Content Wt%
Untreated ZN catalyst	2.66
ZN/TEA (Al/Ti = 10)	1.81
ZN/TEA (Al/Ti = 30)	1.77
ZN/TEA (Al/Ti = 50)	1.73

*0.1 g catalyst treated with 5, 15and 25 mL TEA (1 molar in toluene).

results are taken from the ICP and EDX analyses. Again another important finding was the outstanding role of temperature in the zirconocene catalyst loading on the Ziegler-Natta catalyst. It is clear from Figure 3 that, as the temperature goes up the amount of loading of Zr goes up considerably.

Finally, two other types of catalysts were synthesized in which TIBA or MAO was used as the coupling agent. The reaction conditions were chosen the same as the cases for TEA that resulted in the maximum loading (i.e. Temp: 60°C, AlR₃: 5 mmol, ZN catalyst: 1 g and metallocene catalyst 0.1 g). Table 8 shows the Zr content of the catalysts made. As is clear from the table, the maximum metallocene loading was obtained for TEA cases.

The FTIR analysis of the treated samples showed no special changes in the peak positions, especially C=O stretching peak appearing at 1615 cm⁻¹ (corresponding to diisobutyl phthalate internal donor), after reacting with different types of aluminum alkyls.

This observation indicates that some of DIBP molecules are so tightly complexed to the catalyst surface that they cannot be readily removed by treating with alkyl aluminums and high temperatures [43]. This observation, as we will see later, is completely confirmed by ¹H-NMR analysis of the catalyst. Another finding is that, we can make sure that AlR₃ cannot make any stable compound with the carbonyl groups of the complexed DIBP molecules; or any

probable formed complexes has changed to several Al alkoxide species in the presence of excess AlR₃; this hypothesis is discussed elsewhere [43].

¹H NMR analysis of the treated samples with TEA, TIBA, and MAO showed a decrease in the DIBP content of the catalysts. Table 9 shows the content of DIBP in each of the catalysts. The integral of aromatic region was chosen as the base of comparison.

As is clear from the table, the ability of each of the aluminum compounds in removing DIBP from the ZN catalyst was as follows: MAO>TEA>TIBA. TEA is less bulky and more reactive than TIBA, therefore it could diffuse more readily and react more vigorously than TIBA and therefore the amount of removed DIBP went up. The higher ability of MAO in removing DIBP can be due to the TMA (trimethylaluminum) present, which is more reactive and less bulky than the other two reagents.

According to these results, another reason for a higher loading of the zirconocene on ZN catalyst after treatment with AlR₃ may be the more vacant sites produced on a ZN catalyst surface due to removal of large amounts of DIBP from the catalyst surface. The Cl atoms of the metallocene catalyst then can share their electrons with Mg atoms. Although MAO was able to remove more DIBP from the catalyst (perhaps because of its TMA content), the Zr loading was lower than TEA cases. This may be due to the higher bulkiness of MAO molecules that may inhibit more penetration of the metallocene component into the ZN
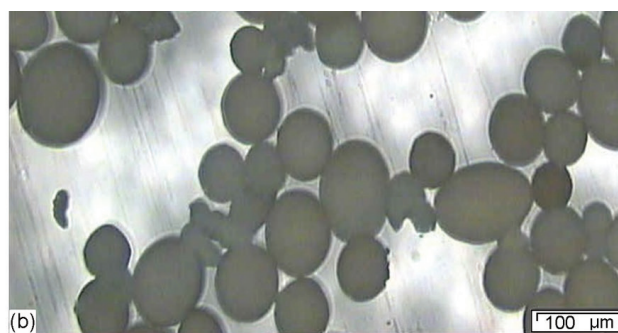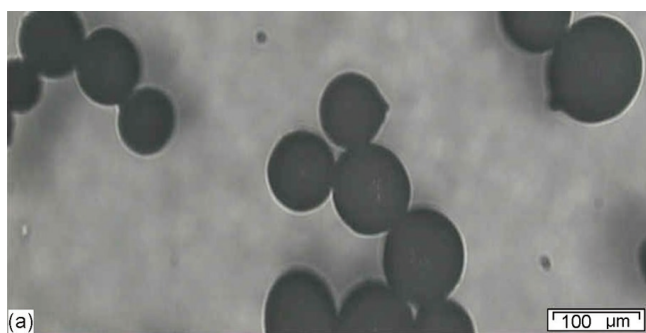
Figure 4. (a) Morphology of the ZN catalyst before treatments, (b) Morphology of the final hybrid catalyst.
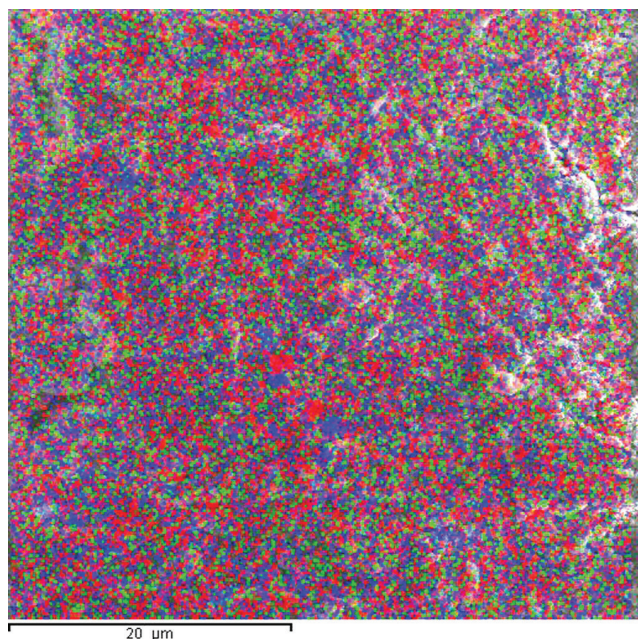
Figure 5. Map of element distributions on the hybrid catalyst surface, Ti (green), Al (red), Zr (blue).

catalyst.

FTIR analysis of the hybrid catalysts also showed no change in the position of the carbonyl group peak; this can be indicative of this fact that, there is no interaction between this functional group and the metallocene catalyst.

UV analysis of the ZN treated catalyst showed that upon treating this catalyst with different amounts of TEA, the changes are merely the same (Table 10).

This observation indicates that the amount of Ti that can be removed from the catalyst is constant which means that only certain types of Ti species are removed from the ZN catalyst by treatment with alkyl aluminums. These produced vacant sites can host the metallocene catalyst [5].

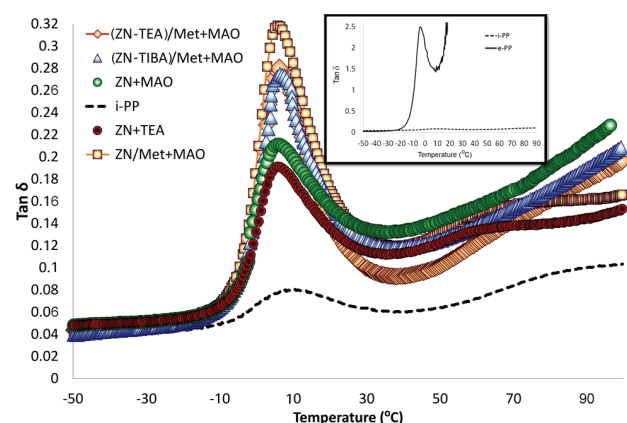Investigating morphologies of the hybrid catalysts

Table 11. Viscometric Molecular Weights (M_v) of Polypropylenes.

Sample	iPP				
	ZN + TEA/ ED	ZN/ TEA	ZN + MAO	(ZN-TEA)/ Met + MAO	(ZN - TIBA)/ Met + MAO
M_v	258000	280000	253000	323000	360000

Polymerization Conditions: Propylene pressure: 6 bar, polymerization media: Toluene, Temperature and time: 15 min at 35ºC and 45 min at 70ºC.

showed that during the two stage reactions the morphologies were retained completely (Figure 4).

In all the cases, the mapping (EDXA) showed a rather homogeneous distribution of each element (Ti, Al and Zr) on the surface of catalyst particles (Figure 5).

Putting together all the results obtained throughout the catalyst part, it can be concluded that the second catalyst is loaded on the first catalyst through three mechanisms:
a. Physical trapping in the pores, cracks and crevices of the ZN catalyst
b. Chemical bonding without any interference from AlR_3
c. Chemical bonding through bridging of the AlR_3 component

Polymer

The polymer reactor blends were studied through DMTA. Their heptane soluble parts were analyzed by DSC. Viscometery was also used to determine the M_v of heptane insoluble (isotactic) fractions.

As is clear from Figure 6, the isotactic PP (having the isotactic index of %97) showed the lowest damping ability (tan δ = 0.08) among all of the synthesized polymers while the full elastomeric PP showed the highest damping ability (tan δ = 2.5). By

Figure 6. DMTA of the polypropylene samples.

Table 12. Activity results of the catalysts.

	Activity (kg PP/g Cat)	II	Activator	$Al_{(MAO)}$/ Zr	Al/ Ti
ZN	5.0	~65%	MAO	-	500
ZN/Met	4.0	~80%	TEA	-	500
ZN/Met	3.0	~50%	MAO	500	500
(ZN-TIBA)/Met	4.0	~50%	MAO	500	
(ZN-TEA)/Met	3.5	~50%	MAO	500	
ZN*	8.0	~97%	TEA	-	

*. In the presence of External Donor (Cyclohexyl(methyl)dimethoxysilane) Al/Si= 20
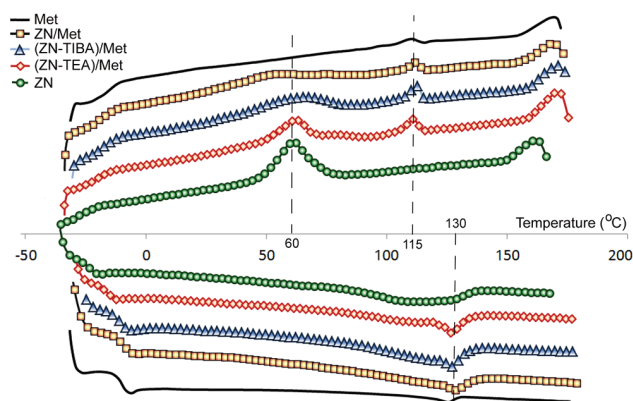
Figure 7. DSC analysis of the heptane soluble parts of polypropylene samples obtained from various catalysts in the presence of MAO as the sole activator. (ZN/TEA and ZN/TIBA showed a thermogram similar to ZN+MAO).

omitting external donor in propylene polymerization (ZN catalyst) the isotactic index decreased from 97% to 72% and the damping factor increased from tan δ = 0.08 to tan δ = 0.19. Finally, by analyzing the polymers obtained from the hybrid catalysts, different damping abilities between those of iPP and ePP were obtained. This analysis, for all the samples, showed just one peak, which is indicative of complete miscibility of all the components: aPP, iPP, and ePP.

For further rationalizing the DMTA results we also moved toward examining the viscometric molecular weights (M_v) of the heptane insoluble parts of the polymers. Table 11 shows the results obtained for the molecular weights.

As is clear from the table, the polymers obtained from the hybrid catalysts show higher M_{vs} than the ones produced by the ZN catalysts. By considering this result along with the results obtained for catalyst activities (Table 12), these can be indicative of a kind of blocking or decreased availability of active sites in the hybrid catalysts. This diminished availability of the active sites also can be due to probable over-reduction of the titanium sites by aluminum alkyl pretreatment of the ZN catalyst producing Ti^{2+} species that are inactive in the polymerization reaction [44]. When the number of active sites decreases, at a constant pressure, monomers go toward the remaining active sites; therefore, the number of monomers in each of the chains and the molecular weight increase. Of course, for better understanding of the quantity and quality of active sites further studies such as stopped-flow polymerization studies are required [45].

DSC analyses of the heptane soluble parts of the polymers are shown in Figure 7 and Table 13. All of

them show a similar pattern. The ones corresponding to the hybrid catalysts show one extra crystallization peak around 115ºC and a melting peak around 130ºC that can be related to the presence of elastomeric PP in the blend.

It should be emphasized that since for the DSC analysis only 5 mg of sample could be used therefore it cannot be a good representative for the amounts of each part present in the mixtures. The only thing that can be said is that, two fractions with different crystallization temperatures are present in the samples which can be indicative of the formation of elastomeric PP (T_c=115±1ºC) and another peak (T_c= 65 ±2ºC) that is perhaps due to the presence of low molecular weight isotactic PPs produced by the ZN part of the hybrid catalyst. Another conclusion is that in the polymers obtained from the hybrid catalysts the ΔH_c and T_c corresponding to the elastomeric part are increased in comparison with the pure elastomeric PP obtained from the pure metallocene catalyst, and also T_m of the pure elastomeric PP is lower than the T_ms observed for the hybrid catalysts. These observations can be indicative of some kind of inhibiting effect of supporting of the (2-PhInd)$_2$ZrCl$_2$ metallocene catalyst on ZN which may have changed the performance of the catalyst in such a way that it produces elastomeric PP with a higher content of isotactic blocks (Scheme 1).

To clarify the effect of the presence of the metallocene catalyst on the performance of the ZN catalyst some further investigations on the heptane soluble parts of some of the polymers were done using ^{13}C NMR analysis. The results are summarized in Table 14. As is clear from the table, the presence of the metallocene catalyst in the polymerization media didn't change the pentad distribution of the heptane soluble parts but the same amount of donor did change the distribution.

Investigations of the effect of bis(2-PhInd)ZrCl$_2$

Table 13. DSC analyses of the heptane soluble parts of the polymers.

	ΔH_m (Tot)$^{(a)}$	M_p (Tot)	$\Delta H_c 1^{(b)}$	$T_c 1$	$\Delta H_c 2^{(b)}$	$T_c 2$
Met	0.46	127	0.53	114	-	-
ZN/Met	5.03	130	1.01	115	3.48	63
ZN/TIBA/Met	10.13	129	2	115	7	67
ZN/TEA/Met	6.3	129	2.1	115	4.05	64
ZN	11.49	wide	-	-	15	64

$^{(a)}$ As is clear from Figure 7 the melting peaks are merged to each other and therefore the enthalpy of fusion of different peaks could not be achieved.
$^{(b)}$ 1 corresponds to higher crystallization peak and 2 to the lower one.

Table 14. Pentad distribution of heptane soluble parts of some of the polymers.

Sample	mmmm	mmmr	rmmr	mmrr	mmrm+rrmr	mrmr	rrrr	rrrm	mrrm
ZN/TEA	28	13	3	14	12	3	11	8	7
ZN/TIBA	28	13	3	14	12	3	11	8	7
ZN/Donor/TEA	21	12	3	14	15	5	13	10	7
ZN/Donor/TIBA	21	12	3	14	15	5	13	10	7
ZN/Met/TEA	29	13	3	13	11	4	10	8	8
ZN/Met/TIBA	29	13	3	14	12	3	10	8	8
Atactic PP	6.25	12.5	6.25	12.5	25	12.5	6.25	12.5	6.25

metallocene catalyst on the behavior of the ZN catalyst showed that although the metallocene catalyst decreased the heptane soluble part of the produced polymer considerably (I.I.% [Isotactic Index] increased from 72 to 80) but we did not see any special change in the heptad distribution of the heptane soluble parts(ZN/TEA and ZN/Met/TEA). This can be indicative of the presence of some kind of barrier that may be caused by the metallocene catalyst inhibiting the aluminum alkyl co-catalyst from reaching polymerization sites on ZN catalyst particles. Therefore by reducing the intensity of the polymerization reaction the I.I.% is increased.

CONCLUSIONS

Precise investigation of a new type of method in making a hybrid Ziegler-Natta/metallocene catalyst clarified several interesting facts, and even by using an experimental design in making such catalysts the importance of different factors was determined. The findings are as follows:

1. In making hybrid catalysts pretreatment of Ziegler-Natta catalyst with an aluminum alkyl enhances the amount of metallocene loading;
2. The amount of aluminum alkyl is a crucial factor on the amount of metallocene loading, if the amount of aluminum alkyl exceeds a specific amount, the amount of metallocene starts to decrease;
3. Three different factors were studied in making the hybrid catalyst including aluminum alkyl concentration, metallocene concentration, and temperature. Temperature appeared to be the most effective factor in the amount of metallocene loading.
4. ^{1}H NMR studies showed that upon reacting the Ziegler-Natta catalyst with aluminum alkyls a large amount of internal donor (i.e., DIBP) is removed from the catalyst; MAO was the strongest

in removing the donor perhaps because of its TMA content.
5. Finally, polypropylene blends were synthesized using the hybrid catalysts and different fractions of the blend were characterized completely. The primitive data indicated that supporting the metallocene catalyst on the ZN catalyst could cause it to produce polymers with higher isotactic block content.

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