Highly Active Ziegler–Natta Catalyst for Propylene Polymerization

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ABSTRACT: Polymerization of propylene was carried out by using a $MgCl_2$–EtOH–$TiCl_4$–ID–TEA–ED catalyst system in *n*-heptane, where ID (internal donor) was an organic diester, ED (external donor) was a silane compound, and TEA (triethyl aluminum) was the activator. The influences of temperature, pressure, time, hydrogen, and the molar ratios of Al/Ti and ED/Ti on polymer isotacticity and catalyst activity were studied by solubility in boiling *n*-heptane and measuring the polymer produced, respectively. The morphology of the polymers was evaluated through scanning electron microscopy and particle size distribution. The rheological properties of the poly(propylene) were determined by the melt flow index. It was found that the catalyst showed good morphology and high activity and also the produced polymers were characterized by high isotacticity and globulelike shapes. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1744–1749, 2005

Key words: Ziegler–Natta polymerization; poly(propylene) (PP); isotactic; catalysts; morphology

INTRODUCTION

Ziegler–Natta catalysts of greatly improved activity and stereoselectivity have been developed using $MgCl_2$ as the support. There are many ways to prepare $MgCl_2$ having high surface area, such as ball-milling, precipitation of soluble $MgCl_2$ complex, reaction of magnesium alkoxides and aryls with $TiCl_4$, and the other titanium compounds as the catalysts and diisobutyl phthalate (DIBP) as the internal donor (ID). These catalysts are cocatalyzed by triethyl aluminum (TEA) plus an external donor (ED), which is usually an organic monoester such as ethyl benzoate, *p*-toluate, or silanes such as cyclohexylmethyl dimethoxysilane (cHMDMS), phenyl triethoxysilane (PTES), and so on.[1–14] These catalyst systems, the most commonly used in current industrial processes, promote high activity and stereoselectivity. In addition to activity and stereoselectivity of the catalysts, the control of size and shape of catalysts is a very important factor because it has a determinative role in the control of morphology of the resulting polymer particles; on the other hand, the spherical and globular shapes of catalysts and polymers are the best. Also, the key point for the preparation of these kinds of catalyst particles is the support preparation that can be produced by $MgCl_2$ alcoholized.[6,7]

The present article reports on $MgCl_2$/EtOH/ID/$TiCl_4$ catalyst system, where $MgCl_2$/EtOH and DIBP were used as support and ID, respectively. Also, results of the investigation on the polymerization conditions and various silane compounds are reported herein. The characterization of the resulting products is also reported; such results can be of interest for producing poly(propylene) (PP) by this type of catalysts, especially for commercial production.

EXPERIMENTAL

Materials

Propylene (polymer grade), nitrogen ($>$99.99%), and *n*-hexane ($H_2O < 2$ ppm) were purchased from Arak Petrochemical Co. (Arak, Iran). $TiCl_4$, TEA, and silanes were purchased from Fluka Chemie (Buchs, Switzerland). DIBP, EtOH, kerosene, and toluene (extrapure grade) were purchased from Merck Co. (Darmstadt, Germany). Anhydrous magnesium chloride and *n*-heptane ($H_2O < 3$ ppm) were obtained from Toho Titanium Co. (Kanagawa, Japan) and Shazand Arak Refining Co. (Tehran, Iran), respectively.

Support preparation

To a 1.0-L flat-bottom flask, equipped with an inert tube for N_2 with 250 mL kerosene at 10°C, were added 5 g anhydrous $MgCl_2$ and 8.2 g EtOH. The mixture was vigorously stirred with a mechanical stirrer while

TABLE I
Effect of Temperature on Catalyst Activity
and Polymer Isotacticity[a]

Parameter	Temperature (°C)				
	60	65	70	75	80
Activity (kg PP/g Ti)	180.3	230.8	256.5	278.7	210.1
I.I.[b] (wt %)	92.5	92.7	92.5	91.9	90.6

[a] Polymerization conditions: monomer pressure (P_m) = 8 bar; time = 2 h; PH_2 = 0; TEA/Ti = 600; ED = cHMDMS; ED/Ti = 40.
[b] I.I., isotactic index.

TABLE II
Effect of Pressure on Catalyst Activity
and Polymer Isotacticity[a]

Parameter	Pressure, P (bar)				
	5	6	7	8	9
Activity (kgPP/g Ti)	116.8	128	197.5	256.5	316.1
I.I. (wt %)	88.0	91.3	92.3	92.5	92.6

[a] Polymerization conditions: temperature = 70°C; time = 2 h; PH_2 = 0; TEA/Ti = 600; ED = cHMDMS; ED/Ti = 40.

the temperature was increased to 70°C. After 10 min, the mixture was transferred to a 1.0-L flask containing 500 mL isoparaffin at −20°C. The precipitate was filtered and then washed three times with 100 mL anhydrous n-hexane.[3,8,14] The support was dried and stored under N_2 atmosphere.

Catalyst preparation

To a 1.0-L flat-bottom flask were added 5 g of the prepared support and 50 mL toluene. At 10°C, 50 mL $TiCl_4$ was added dropwise for a period of 0.5 h under vigorous stirring with a mechanical stirrer. The temperature of the mixture was increased to 120°C in 1 h. Upon reaching 80°C, 1.2 mL DIBP as an ID was added.

The temperature was maintained at 120°C for 2 h; the mixture was then left to decant and afterward the hot liquid was siphoned off. The solid product was treated with 50 mL $TiCl_4$ for 2 h. Finally, it was allowed to settle and the liquid was siphoned off while hot; the residual solid was washed 10 times with 100 mL hot n-hexane until no traces of titanium were detected in the washing liquid.[3–9,15]

Polymerization

Polymerization was carried out in a 1.6-L steel-jacket Buchi autoclave reactor (Reactor Vessels Ltd., Kent, UK), equipped with a mechanical seal stirrer in the slurry phase.

After depletion of all moisture and oxygen by nitrogen, 800 mL of n-heptane was added and then mixed for 10 min. The order of addition of prescribed amounts of the three compounds was: TEA, ED, and 20 mg of catalyst (dispersed in 2 mL n-heptane) by using glass syringes. Before the catalyst addition, TEA and ED were precontacted for 5 min. The reactor was warmed to the required temperature (Table I) and then propylene was supplied continuously at the required pressure and time (Tables II and III, respectively). In the polymerization in which hydrogen was used, hydrogen was injected at the required amount

(Table IV) by using a Buchi pressure-flow gas controller before propylene was supplied.

After the polymerization, the untreated gases were slowly released and the polymer was then filtered and dried *in vacuo* at 70°C overnight to a constant weight.

Analysis

The amounts of titanium and magnesium elements in the prepared catalyst were determined by use of an atomic absorption spectrophotometer (Shimadzu 6800, Kyoto, Japan). A precisely weighed quantity of catalyst (∼ 100–150 mg) was dissolved in 10 mL of 0.1M sulfuric acid solution and diluted to 100 mL with distilled water.[5,15] The chloride content was evaluated according to Volhard's method (Table V).[15]

Polymer fractionation

The atactic fraction of polymers was measured by extracting the polymers for 5 h with boiling n-heptane in a Soxhlet-type apparatus. The boiling-insoluble fraction was isotactic PP and the boiling-soluble fraction was atactic. The recovered fractions were dried *in vacuo* at 70°C to constant weight. The wt % of n-heptane–insoluble polymer in a whole sample is referred to as the isotactic index (I.I.).[16,17]

Characterization

Morphologies of the support alcoholized, catalyst, and polymers were depicted using SEM (Stereoscan 360; Cambridge Instruments, Cambridge, UK) under an inert atmosphere. The surface area, pore volume, and pore radius of support, alcoholized support, and cat-

TABLE III
Effect of Time on Polymer Isotacticity[a]

Parameter	Time (h)				
	1	1.5	2	2.5	3
I.I. (wt %)	92.2	92.8	92.5	92.3	93.1

[a] Polymerization conditions: temperature = 70°C; P_m = 8 bar; PH_2 = 0; TEA/Ti = 600; ED = cHMDMS; ED/Ti = 40.

TABLE IV
Effect of H_2 on Catalyst Activity
and Polymer Isotacticity[a]

Amount of H_2 (mL)	Activity (kg PP/g Ti)	I.I. (wt %)	MFI (230°C/2.16 kg)
0	256.5	92.5	0.57
57	316.7	92.6	3.7
95	362.2	91.8	5.4
153	490.5	92.1	10.1
202	594.4	92.5	14.3

[a] Polymerization conditions: temperature = 70°C; P_m = 8 bar; time = 2 h; TEA/Ti = 600; ED = cHMDMS; ED/Ti = 40.

alyst were measured by using the BET (Brunauer–Emmett–Teller) method (NOVA 2000, Quantachrome Instruments, Boynton Beach, FL).[18]

Catalyst activity was determined in terms of the produced poly(propylene) (kg) per the amount of Ti used (g) in the polymerization. The distribution of gain size and melt flow index (MFI, g/10 min) of polymers were determined using a particle sizer (Retsch Inc., Newtown, PA), by seizing, and a Model 4100 apparatus (Zwick, Bamberg, Germany; ASTM D 1238), respectively.[19]

RESULTS AND DISCUSSION

According to the literature, the best molar ratio of EtOH/MgCl$_2$ is between 2 and 3.5 (preferably, 2.7–3).[3] For this reason, the ratio of EtOH/MgCl$_2$ was selected to be about 2.8. Table V shows the elemental analysis and BET surface area of support, support alcoholized, and catalyst. According to Table V, the alcoholization has substantially increased the surface area of support. The percentage of Mg, Cl, and Ti in the catalyst was 16.86, 59.12, and 2.57, respectively.

Catalyst activity and stereospecificity of PP are sensitive to polymerization temperature, monomer pressure, TEA/Ti and ED/Ti ratios, hydrogen, and type of silane (Tables I–IV and VI–VIII).

TABLE VI
Effect of TEA/Ti Ratio on Catalyst Activity
and Polymer Isotacticity[a]

| Parameter | TEA/Ti ratio | | | | |
	400	500	600	700	800
Activity (kg PP/g Ti)	190.4	210.5	256.5	208	196.9
I.I. (wt %)	92.4	94.8	92.5	89.8	88.4

[a] Polymerization conditions: temperature = 70°C; P_m = 8 bar; time = 2 h; PH_2 = 0; ED = cHMDMS; ED/Ti = 40.

According to Table I, the activity and stereoselectivity of the catalyst gave a maximum at 65–75°C and then decreased with increasing temperature. That result might be ascribed to a destruction of active sites at the higher temperature in the polymerization condition because this process is irreversible in nature.[20] As Table II shows, the catalyst activity and polymer isotacticity increased as the monomer pressure increased.

The dependency of catalyst activity and stereospecificity of polymers on the ratio of TEA/Ti is shown in Table VI. The maximum activity of catalyst was observed at the molar ratio TEA/Ti of 600, whereas, the maximum selectivity was observed at that of 500. At the high ratio of TEA/Ti, there was a decrease in catalyst activity and stereoselectivity because a reduction of Ti^{+4} to Ti^{+2} occurred, given that these species are not active for propylene polymerization.[21–23]

The type of silane affects the propylene polymerization activity and catalyst stereoselectivity.[24,25] Table VII shows the results obtained for the catalyst activity and polymer isotacticity with the MgCl$_2$/EtOH/TiCl$_4$/ID/TEA/ED catalyst system for the different external donors. The highest values of catalyst activity and polymer stereospecificity were attained with cHMDMS compared to those of the three other silanes. This result could be explained by the presence of the bulk cyclohexyl group in cHMDMS that is important for the selective poisoning of the nonselective sites in the catalyst. Meanwhile, the cyclohexyl group is more effective than the phenyl group (Table VII). According to Table VIII, the catalyst activity and se-

TABLE V
Effect of Alcoholization on Support
and Catalyst Properties

| Parameter | Compound | | |
	MgCl$_2$	Support alcoholized	Catalyst
Surface area (m^2/g)	62.56	146.61	151.46
Porosity (cm^3/g)	0.084	0.471	0.413
Average pore radius (Å)	88.42	64.44	54.51
Ti (wt %)	—	—	2.57
Mg (wt %)	25.20	11.31	16.86
Cl (wt %)	73.73	29.53	59.12

TABLE VII
Effect of Different Silanes on Catalyst Activity
and Polymer Isotacticity[a]

| Parameter | ED | | | |
	TES[b]	PTES	cHMDMS	DCDMS[c]
Activity (kg PP/g Ti)	216.6	188.7	256.5	130.8
I.I. (wt %)	86.3	92.3	92.5	80.5

[a] Polymerization conditions: temperature = 70°C; P_m = 8 bar; time = 2 h; PH_2 = 0; TEA/Ti = 600; ED/Ti = 40.
[b] TES, tetraethoxysilane.
[c] DCDMS, dichlorodimethylsilane.

TABLE VIII
Effect of ED/Ti Ratio on Catalyst Activity
and Polymer Isotacticity[a]

Parameter	ED/Ti ratio				
	10	20	30	40	50
Activity (kg PP/g Ti)	200.4	216.3	230.3	256.5	228.8
I.I. (wt %)	86.2	87.9	93.3	92.5	92.0

[a] Polymerization conditions: temperature = 70°C; P_m = 8 bar; time = 2 h; PH_2 = 0; ED = cHMDMS; TEA/Ti = 600.

lectivity increased as the molar ratio of ED/Ti increased.

The isotacticity of polymer is approximately constant with an increase in the polymerization time (Table III).[26,27] As shown in Figure 1, the catalyst yield increases as the time of polymerization increases. The selected time of polymerization was 1, 1.5, 2, 2.5, and 3 h under the same condition.

Hydrogen is used for controlling molecular weight as a chain-transfer agent. Table IV shows the effects of hydrogen on the catalyst activity and polymer isotacticity. The catalyst activity in the absence of hydrogen was around 256.5 kg PP/g Ti that, in the presence of hydrogen, was enhanced more than twofold (594.4 kg PP/g Ti). It has been proposed in the literature as an explanation for such enhancement of the catalyst activity that a regioirregular (2,1-) insertion of propylene into the growing chain produces a species that has a very low reactivity with respect to further propagation and that effectively remains dormant until chain transfer with hydrogen takes place.[25,28–32] The I.I. values were not influenced by the addition of hydrogen to the polymerization system.

According to Figure 2, the diameter of most of the polymers is >125 μm and the majority of the particles fall into the 125- to 355-μm range.
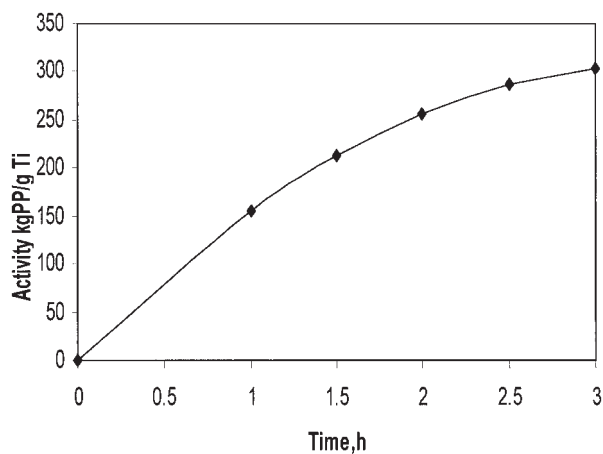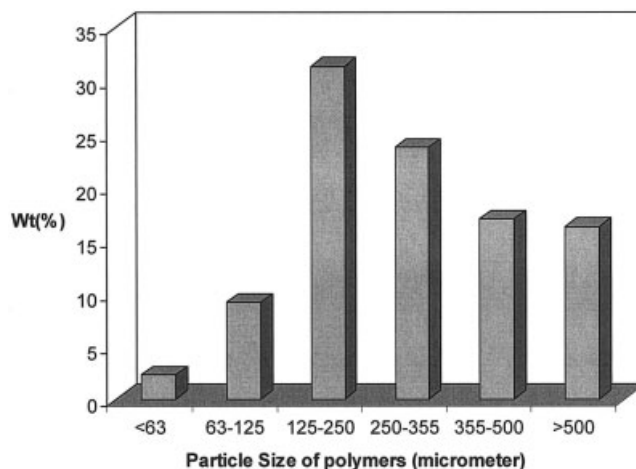

Figure 2 Particle size distribution of polymers.

Polymer characterization

MFI

The rheological properties of the polymers were studied by the melt flow index (MFI). As observed from Table IV, MFI increases by addition of H_2 because the molecular weight decreases.

Surface characteristics of support, catalyst, and PP

It has been found that the shape of support is more critical than the catalyst shape. On the other hand, both activity and texture of the catalyst affect the polymer morphology; moreover, the polymerization catalysts are well known to replicate their morphology into the polymer particles. In other words, the catalyst particle acts as a template for growth of the polymer particle.[3,33,34] Although the polymer particle replicates the morphology of the catalyst particle, the catalyst particle breaks down or shatters during the polymerization process and the fragments become dispersed throughout the polymer particle.[35]

SEM was used to study the morphologies of the support, catalyst, and polymers (Fig. 3). As Figure 3(a) shows, the support alcoholized particles have a spherical shape. The morphology of both the catalyst and the polymers is a small globulelike structure [Fig. 3(b) and (c)].

CONCLUSIONS

The $MgCl_2$/EtOH/$TiCl_4$/ID/TEA/ED catalyst system has shown high stereoselectivity and activity. This catalyst system has a high surface area and also the $MgCl_2$ alcoholized has more surface area than that of $MgCl_2$.
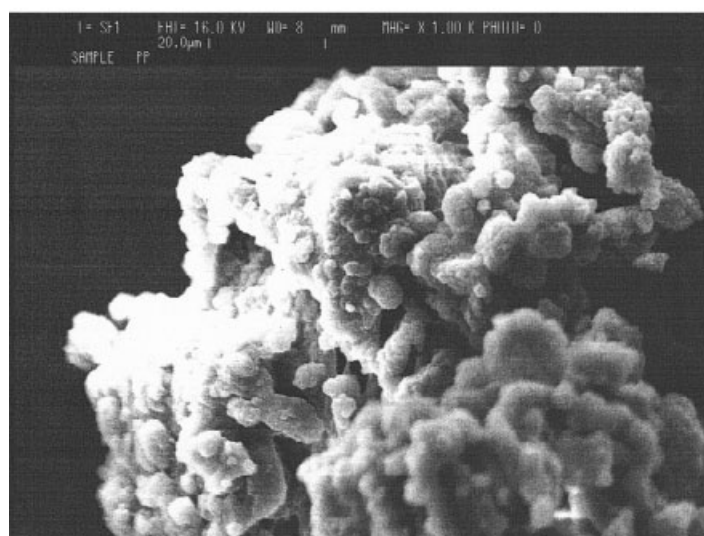
The optimum activity of the catalyst is at 70–75°C, a pressure of >8 bar, and 600 and 40 molar ratios of

Figure 1 Effect of time on the catalyst activity.

(a)
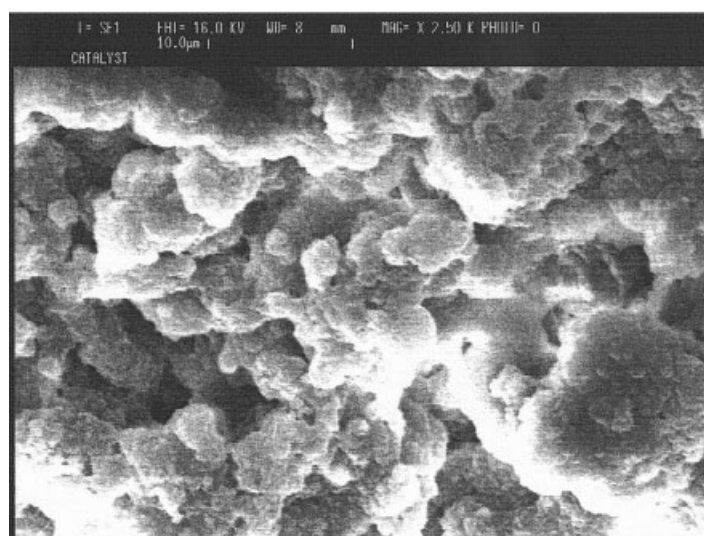
(b)

(c)

Figure 3 SEM micrographs of (a) support alcoholized; (b) catalyst; (c) poly(propylene).

TEA/Ti and ED/Ti, respectively. cHMDMS has been found to be a more effective electron donor than TES, DCDMS, or PTES. The increase of MFI shows that the molecular weight of polymers has decreased with increasing amount of H_2, but the activity of catalyst increased. Meanwhile, the addition of hydrogen did not have any noticeable effect on the catalyst stereoselectivity. The morphology of the catalysts and polymers was a globulelike structure.

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