Copolymerization of Ethylene and Propylene Catalyzed by Novel Magnesium Chloride Supported, Vanadium-Based Catalysts

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ABSTRACT: Two novel magnesium chloride supported, vanadium-based Ziegler–Natta catalysts with 9,9-bis(methoxymethyl)fluorene and di-*i*-butyl phthalate as internal donors were prepared and used in the copolymerization of ethylene and propylene. The catalytic behaviors of these catalysts were investigated and compared with those of traditional magnesium chloride supported, vanadium-based catalysts without internal donors. Differential scanning calorimetry, gel permeation chromatography, and ^{13}C-NMR spectroscopy analysis were performed to characterize the melting temperatures, molecular weights, and molecular weight distributions as well as structures and compositions of the products. The copolymerization kinetic results indicated that the novel catalyst with 9,9-bis(methoxymethyl)fluorene as an internal donor had the highest catalytic activity and optimal kinetic behavior in ethylene–propylene copolymerization with an ethylene/propylene molar ratio of 44/56. Low-crystallinity and high-molecular-weight copolymers were obtained with these novel magnesium chloride supported, vanadium-based catalysts. The reactivity ratio data indicated that the catalytic systems had a tendency to produce random ethylene–propylene copolymers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2625–2629, 2009

Key words: catalysts; polyolefins; Ziegler–Natta polymerization

INTRODUCTION

In the area of Ziegler–Natta olefin polymerization, vanadium-based catalysts, which have the important characteristic of producing amorphous or elastomeric products, are unique in their ability to incorporate ethylene and propylene monomers in a random order.[1,2] Comparably, the traditional heterogeneous titanium catalysts used for the copolymerization of ethylene and propylene produce copolymers with relatively long ethylene sequences. It is impossible to produce ethylene–propylene (EP) copolymers with properties similar to those obtained with vanadium catalysts,[3] but the low activity of vanadium catalytic systems limits their further application. It is of great importance to develop a high-efficiency supported vanadium-based catalyst for the copolymerization of ethylene and propylene.

It is well known that the catalytic activity of heterogeneous catalysts depends on the character of the support and its textural structure.[4–6] Magnesium complexes and internal donors play important roles in Ziegler–Natta titanium catalysts. For vanadium catalysts based on vanadium oxytrichloride[7] and vanadium tetrachloride (VCl$_4$),[8] a magnesium complex as a support can stabilize the active sites and improve the activity in polymerization. 1,3-diether and phthalate, used as internal donors, are known to produce highly active and highly stereospecific catalyst components for propylene polymerization. In this study, two novel vanadium-based Ziegler–Natta catalysts with 9,9-bis(methoxymethyl)fluorene (BMMF) and di-*i*-butyl phthalate (DIBP) as internal donors were prepared. The effects of reaction conditions on the polymerization behaviors and properties of the products were investigated.

EXPERIMENTAL

All operations were carried out under highly pure nitrogen with standard Schlenk techniques.

Materials

Polymerization-grade ethylene, propylene, and highly pure nitrogen, supplied by Daqing Petrochemical Co., Ltd., were used after passage through a 4-Å molecular sieve (Fluka Chemical Corp., Buchs, Switzerland). Triethylaluminum (AlEt$_3$; Ethyl Co., Houston, TX; 95% purity) was used without further purification. VCl$_4$, DIBP, *n*-hexane, and anhydrous magnesium chloride (MgCl$_2$) were obtained from Beijing

Chemistry Reagents Co., Ltd. (Beijing, China). MgCl$_2$·2.56C$_2$H$_5$OH[9] and BMMF[10] were prepared according to methods described in the literature.

Preparation of the catalyst

Excess VCl$_4$ was injected into a dried Schlenk reactor under the protection of nitrogen and cooled to −20°C; then, a given amount of MgCl$_2$·2.56C$_2$H$_5$OH complex was added, and the temperature was increased to 60°C. Subsequently, an internal donor was added to the reactor with an MgCl$_2$/internal donor molar ratio of 10 : 1. The temperature was increased to 120°C in 2 h, this temperature was held for 2 h, and the solid components were separated by filtration. For a second time, excess VCl$_4$ was injected into the dried Schlenk reactor again, and the temperature was kept at 110°C for 2 h; then, the solid components were separated again by filtration. Finally, the solid components were washed five times with n-hexane at 60°C, and the catalyst was dried in vacuo. BMMF and DIBP as internal donors were used to prepare the MgCl$_2$/VCl$_4$/BMMF (V$_{content}$ = 4.84 wt %) and MgCl$_2$/VCl$_4$/DIBP (V$_{content}$ = 5.05 wt %) catalysts. Similarly, the aforementioned procedures were repeated, but no internal donor was added in the process of preparing the MgCl$_2$/VCl$_4$ catalyst (V$_{content}$ = 3.25 wt %).

Polymerization

Polymerization was carried out in a 250-mL glass reactor equipped with a mechanical stirrer by a continuous-purge copolymerization method.[11] The solubility of the monomers strictly obeyed Henry's law and could be controlled by the partial pressure of each monomer. n-Hexane as a solvent (100 mL) was saturated with an ethylene–propylene gas mixture at a regulated temperature (controlled by a DF-101S heat-collected constant-temperature stirrer, Jiangsu Zhengji Instrumental Co., Jintan, China). After saturation, the reaction was initiated by the introduction of the AlEt$_3$ cocatalyst and the catalyst precursors. The reactor was kept at a constant pressure (controlled with a BY-U differential pressure meter, Cewei Instrumental Co., Shanghai, China) by the continuous addition of an ethylene–propylene gas mixture. About 30 min later, the reaction was stopped through the addition of an acidic methanol solution, the products were subsequently filtered off and washed with methanol, and then they were dried in vacuo at 60°C for 12 h.

Characterization of the products

The weight-average molecular weight (M_w) and molecular weight distribution (MWD) of the EP copolymer were determined with a Waters Alliance (Freehold, NJ) GPCV-2000 equipped with a refractive-index detector at 150°C with three Polymer Laboratory (Amherst, MA) mixed-B columns and 1,2,4-trichlorobenzene as the solvent. The number-average molecular weight (M_n) and M_w were determined with polystyrene standard calibration as a reference. The melting temperature and enthalpy of fusion of the EP copolymer were measured on a PerkinElmer (Waltham, MA) DSC-7 differential scanning calorimeter in the following manner. First, the sample was heated to 210°C at 10°C/min and held there for 5 min to remove the thermal history. Then, it was cooled to 50°C at 10°C/min, and this was followed by reheating at 10°C/min. The thermogram of each sample was recorded in the second heating run. ^{13}C-NMR spectra of the EP copolymer were measured on a Bruker (Fällanden, Switzerland) DMX-400 NMR spectrometer at 75 MHz. o-Dichlorobenzene-d_4 was used as a solvent, and the concentration of the sample was 10 wt %. The spectra were recorded at 120°C with hexamethyldisiloxane as an internal reference, and about 3000 transients were collected.

RESULTS AND DISCUSSION

The properties of the copolymer are controlled by all the components of the catalytic systems,[12] that is, the support, the Lewis base, and the growing polymer chain. These components can modify the acidity of the transition-metal atom,[13] create steric hindrance around it, or influence the behavior of the active sites. In addition to the catalytic system used, the properties of an EP copolymer significantly depend on the contents of the comonomers and their distributions, which depend essentially on the polymerization conditions in turn.[14] To obtain a copolymer with a defined composition, the reaction conditions have to be kept constant for the entire polymerization process.[15]

Effects of the ethylene/propylene (E/P) molar ratio on the catalytic activity

The E/P molar ratio has an important influence on the catalytic activity and properties of the copolymer. To examine the optimal monomer ratio, polymerization was carried out with different E/P molar ratios, and the optimal activity of each experimental point is shown in Table I. The E/P molar ratio varied from 10/90 to 80/20 in the polymerization.

The catalytic activity increased with an increase in the E/P molar ratio, and the maximum catalytic activity appeared at E/P = 80/20 for the MgCl$_2$/VCl$_4$/BMMF catalytic system. For the MgCl$_2$/VCl$_4$/DIBP catalytic system, it was independent of the E/P molar ratio. For the MgCl$_2$/VCl$_4$ system, the catalytic activity presented a peak value with the E/P

TABLE I
Effects of the E/P Molar Ratio on the Catalytic Activity

E/P (mol/mol)	Activity (g of EPR/g of catalyst h)		
	$MgCl_2/$ $VCl_4/BMMF$	$MgCl_2/$ $VCl_4/DIBP$	$MgCl_2/$ VCl_4
10/90	19.5	28.2	4.2
30/70	26.3	27.0	5.5
44/56	26.2	26.0	9.1
60/40	34.7	27.0	11.5
80/20	40.1	26.9	9.0

Polymerization conditions: catalyst loading = 0.1 g; Al/V = 100; temperature = 20°C; solvent = hexane; and time = 30 min.

EPR, ethylene-propylene rubber.

molar ratio increasing. The high catalytic activity can be attributed to the activation of dormant catalyst sites by ethylene and the high insertion rate of ethylene[16] during polymerization. It is noteworthy that the catalysts containing internal donors showed higher activity than the $MgCl_2/VCl_4$ system. It can be concluded that internal donors play an important role in stabilizing the active centers.

Kinetics of polymerization with different catalytic systems

To understand the catalytic systems better, the kinetic data, which indicate the polymerization rate versus time with an E/P molar ratio of 44/56, are given in Figure 1. All the activity curves show decay, and they became stable gradually during polymerization. This high activity in the initial stage may be explained as follows: the concentration of the catalyst was higher, and the active centers activated by $AlEt_3$ were more numerous. With the progress of the reaction, the concentration of the catalyst and active sites was reduced, so the activity
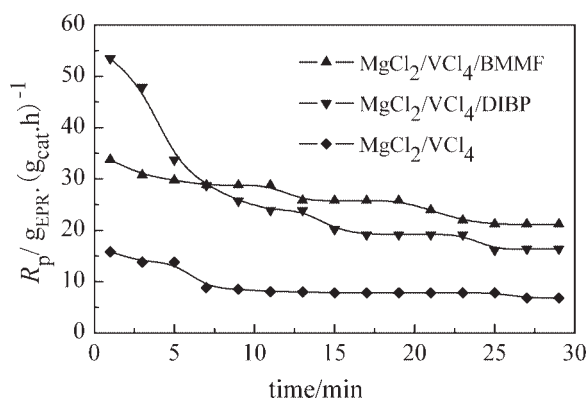
Figure 1 Kinetic curves of polymerization with an E/P molar ratio of 44/56 (R_p = rate of polymerization; EPR = ethylene-propylene rubber; polymerization conditions: catalyst loading = 0.1 g; Al/V = 100; temperature = 20°C; solvent = hexane; and time = 30 min).

decreased to some extent. More importantly, diffusion limitations were more dominant in the initial stage of polymerization. The coating of the catalyst surface with the polymer resulted in a high initial polymerization rate; this was followed by an induction period as the coating limited the diffusion of the monomers.[17]

It must be stressed that the heterogeneous catalysts with internal donors showed higher catalytic activity than the $MgCl_2/VCl_4$ catalyst. It is thought that the advantage of an internal donor may be its capability via functional groups to Lewis acid sites in the catalytic system. The $MgCl_2/VCl_4/BMMF$ catalyst presented more stable kinetic behavior.

Functions of internal donors

According to the aforementioned results, the $MgCl_2/VCl_4/BMMF$ system offers better behavior than the $MgCl_2/VCl_4/DIBP$ system in polymerization. The configurations of the two internal donors are given in Figure 2. It can be concluded that BMMF plays a more important role in improving the catalytic activity. This may be related to the structures of BMMF and DIBP: the distance of two oxygen atoms in BMMF is about 3×10^{-10} m, whereas the distance in DIBP is 5×10^{-10} m. This distance of 3×10^{-10} m is appropriate for firmly incorporating vanadium compounds and keeping the catalytic activity higher.[18] On the basis of the structures of BMMF, the C9 atom on the fluorenyl ring bridge-bonded the two methoxymethyls in the sp^3 hybrid orbitals, and this made the fluorenyl ring rotate with difficulty, so the conformation number was smaller. This special structure may contribute to the high efficiency of the $MgCl_2/VCl_4/BMMF$ catalyst.

For the $MgCl_2/VCl_4/DIBP$ system, DIBP (ca. 20 wt %) and VCl_4 can form a 1 : 1 complex with DIBP, acting as bidentate ligands: both of their carbonyl groups are coordinated to the same vanadium atom. Meanwhile, the dominant component is the complex of $MgCl_2$ with DIBP.[19] An earlier analysis indicated
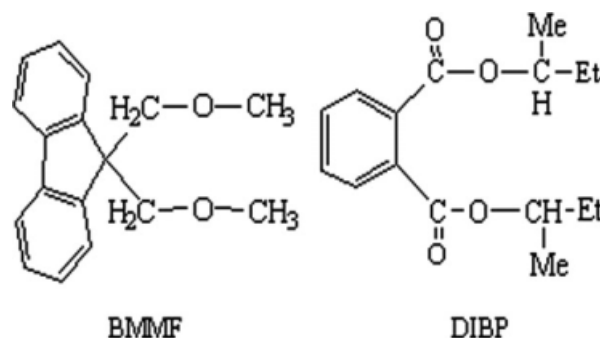
Figure 2 Configuration of the two internal donors.

TABLE II
Gel Permeation Chromatography Results for the Copolymers with Ethylene Contents of 71.07, 67.90, and 53.04 mol %

Catalyst	M_n (10^5)	M_w (10^6)	MWD
MgCl$_2$/VCl$_4$/BMMF	1.0	1.2	11.8
MgCl$_2$/VCl$_4$/DIBP	1.4	1.2	8.7
MgCl$_2$/VCl$_4$	1.1	1.1	10.4

Polymerization conditions: catalyst loading = 0.1 g; Al/V = 100; temperature = 20°C; E/P = 44/56; solvent = hexane; and time = 30 min.

that contact between ester-based catalysts and cocatalysts containing AlEt$_3$ results in the removal of a large fraction of the esters from the solid surfaces, which leads to the reduction of the active center. Only the complex within the solid catalyst improves the activity.[20]

Gel permeation chromatography analysis of the copolymer

The molecular weight was one important factor in determining the mechanical and rheological properties of the polymers. The M_w and MWD values of the copolymers with ethylene contents of 71.07, 67.90, and 53.04 mol % were measured with gel permeation chromatography. The results are illustrated in Table II.

All the polymers produced by supported catalysts had a high molecular weight and wide MWD. This can be explained as follows: the activation energies of chain transfer and deactivation reactions with respect to the propagation reaction were higher.[21] For the supported catalysts, the β-elimination transfer between two active centers was hindered, and this resulted in larger growth of the polymer chain. On the other hand, it is thought that the supported vanadium complex existed in the oxidation of V^{4+} during the preparation of the catalyst. After the treatment with the AlEt$_3$ cocatalyst, most of the vanadium complexes became the ideal active sites

(V^{3+}) by alkylation.[22,23] Because of this heterogeneity of the supported vanadium catalysts, the functions of different active sites were different, and this caused the wider MWD.

No specific trends for M_w and MWD of the polymers can be established from Table II. However, the copolymers obtained with the MgCl$_2$/VCl$_4$/BMMF catalyst presented the widest MWDs in this study. This can be attributed to the interaction of BMMF with vanadium active sites, which needs further investigation. Meanwhile, copolymers from the MgCl$_2$/VCl$_4$ catalyst had the lowest molecular weights. This also indicated that the catalyst containing internal donors kept the sites active for a longer time to promote the growth of the polymer chain.

Differential scanning calorimetry analysis of the copolymer

The crystallinity of the copolymers is shown in Table III. The crystallinity of each sample was calculated with methods from the literature.[24] For EP copolymers with high ethylene contents, such as those obtained in this work, it is also possible to observe the crystallinity. It was found that the crystallinity increased with the E/P molar ratio, and this is consistent with the results reported by Dong et al.[25] It is expected that the crystallinity of an EP copolymer with a higher comonomer composition will be smaller. In this work, the copolymers were practically amorphous (the crystallinity was below 20%).

^{13}C-NMR analysis of the copolymer

^{13}C-NMR can afford more structural information than ^{1}H-NMR in differentiating similar C—C and C—H bonding arrangements in hydrocarbon structures.[26] The ^{13}C-NMR spectra of the copolymer with an E/P molar ratio of 44/56 were determined. All the resonance peaks were assigned with the terminology used by Carman and Wilkes.[27] The composition of the products was estimated from the spectra

TABLE III
Differential Scanning Calorimetry Results for Copolymers Obtained with Different Catalysts

E/P (mol/mol)	BMMF			DIBP		
	T_m (°C)	ΔH_f (J/g)	X_c (%)	T_m (°C)	ΔH_f (J/g)	X_c (%)
10/90	120.5	4.5	1.6	—	—	—
30/70	120.7	21.5	7.4	119.7	21.9	7.5
44/56	120.9	26.9	9.3	119.7	27.1	9.3
60/40	121.4	38.2	13.2	120.4	31.7	10.9
80/20	121.5	54.3	18.7	119.7	53.2	18.3

Polymerization conditions: temperature = 20°C; E/P = 44/56; and Al/V = 100. ΔH_f = enthalpy of fusion; T_m = melting temperature; X_c = crystallinity.

TABLE IV
^{13}C-NMR Analysis of Copolymers Obtained with Different Catalysts

Sequential composition (mol %)	MgCl$_2$/ VCl$_4$/BMMF	MgCl$_2$/ VCl$_4$/DIBP	MgCl$_2$/ VCl$_4$
E	71.07	67.90	53.04
P	28.93	32.10	46.96
EE	43.17	38.39	31.49
EP	54.20	58.38	63.27
PP	2.626	3.231	5.246
EEE	48.33	43.53	32.89
PEE	22.74	24.37	20.15
PPE	28.93	32.10	46.96
r_1	2.03	1.67	1.27
r_2	0.12	0.14	0.21
$r_1 r_2$	0.25	0.24	0.27

Polymerization conditions: temperature = 20°C; E/P = 44/56; and Al/V = 100. E = ethylene; P = propylene; r_1 = reactivity ratio for ethylene; r_2 = reactivity ratio for propylene.

according to the calculation scheme proposed by Randall,[28] and the results are given in Table IV.

The EP copolymers produced with the catalysts containing internal donors had higher ethylene contents than those produced with the MgCl$_2$/VCl$_4$ catalyst. Besides, the MgCl$_2$/VCl$_4$/BMMF catalytic system produced a copolymer with a higher ethylene content than the MgCl$_2$/VCl$_4$/DIBP system with the same E/P molar ratio. This also indicated that the MgCl$_2$/VCl$_4$/BMMF catalyst could insert more ethylene into the polymer chain, and this is the reason for its highest catalytic activity.

The calculated reactivity ratios in Table IV show that the three catalysts produced similar random EP copolymers. By examining the microstructures of the products (monad, dyad, and triad distributions) via ^{13}C-NMR, we determined that the composition is mainly based on the structure and content of the ethylene fragments. Meanwhile, it must be stressed that the ethylene sequence is a key factor that determines the properties of the product.

CONCLUSIONS

Novel MgCl$_2$-supported, vanadium-based catalysts were prepared. By changing the polymerization conditions and analyzing the properties of the polymers synthesized with the three catalysts, we obtained some useful conclusions.

The three vanadium-based catalysts all perform outstandingly for the copolymerization of ethylene and propylene, and the activity is higher with internal donors in the catalyst components because of their interactions with vanadium and magnesium compounds. Compared to the MgCl$_2$/VCl$_4$/DIBP catalyst, the MgCl$_2$/VCl$_4$/BMMF catalyst is more appropriate for producing EP copolymers because of its better polymerization kinetics. According to an analysis of the products, the molecular weights of the copolymers produced in this study were high (10^6 g/mol), and the composition was close to random, although there was a higher ethylene content. Meanwhile, the EP copolymer obtained with the MgCl$_2$/VCl$_4$/BMMF catalyst has a wider MWD, a higher ethylene content, and a higher melting temperature in comparison with that obtained with the MgCl$_2$/VCl$_4$/DIBP catalyst under similar conditions.

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