

COPOLYMERIZATION OF ETHYLENE AND PROPYLENE CATALYZED BY MAGNESIUM CHLORIDE SUPPORTED VANADIUM/TITANIUM BIMETALLIC ZIEGLER-NATTA CATALYSTS*

Tao Jiang^{a, b**}, Hong-xia Chen^a, Chen-gang Cao^a, Guo-liang Mao^b, Wei Du^b and Deng-fei Wang^b

^a College of Material Science and Chemical Engineering, Tianjin University of Science & Technology,
Tianjin 300457, China

^b Department of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, China

Abstract Magnesium chloride supported vanadium/titanium bimetallic Ziegler-Natta catalysts with di-*i*-butyl phthalate as internal donor for copolymerization of ethylene and propylene were prepared. The effects of reaction temperature, ethylene/propylene molar ratio, aluminium/vanadium (Al/V) molar ratio and titanium/vanadium molar ratio on the catalytic activity were investigated. The molecular weight, molecular weight distribution, sequence composition and crystallinity of the products were measured by gel permeation chromatography, ¹³C-NMR and differential scanning calorimetry analysis, respectively. In comparison to the vanadium and titanium catalysts, the bimetallic catalyst showed higher catalytic activity and better copolymerization performance. The obtained ethylene/propylene copolymers have high molecular weight (10⁵), broad molecular weight distribution, high propylene content with random or short blocked sequence structures ($r_{EP} = 1.919$), low melting temperatures and low crystallinities ($X_c < 20\%$).

Keywords: Ziegler-Natta polymerization; Vanadium/titanium catalyst; Ethylene-propylene copolymer.

INTRODUCTION

As a semi-crystalline polymer, polypropylene (PP) is widely used in packaging, textile and automobile industries because of its outstanding processability and mechanical performances. Nevertheless, the applications of PP are severely limited because of its weakness at low temperatures^[1]. To overcome this weakness, a small amount of ethylene can be added to form a copolymer which allows better control of the crystalline process^[2]. Herein, a key is to find a novel catalyst system with good copolymerization ability and high catalytic activity for copolymerization of ethylene and propylene.

Vanadium-based Ziegler-Natta catalysts are unique in their capability to incorporate ethylene and propylene monomers in a random order^[3]. However, the low activity of vanadium catalyst limits its further application. Conversely, the traditional titanium-based Ziegler-Natta catalysts used in copolymerization of ethylene and propylene usually afford high catalytic activity, but the copolymer obtained often bears long ethylene block structures. Therefore, a bimetallic catalyst, which combines the advantages of the two mentioned catalytic systems, was expected to promote the production of ethylene-propylene (EP) copolymers. Previous

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** Corresponding author: Tao Jiang (姜涛), E-mail: jiangtao@tust.edu.cn

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publications^[4–7] described several vanadium/titanium bimetallic catalytic systems, but the levels of residual catalysts were found to be very high, which restricted their applications in copolymerization of ethylene and propylene. Few achievements on the attempt to develop this vanadium/titanium bimetallic Ziegler-Natta catalyst of low-cost but high-efficiency were reported yet. Usually, the immobilization of the Ziegler-Natta catalysts on inorganic carriers is important^[8], since supported catalysts can quickly disperse more active centers. This can increase activity over a longer period and reduce the amount of cocatalyst during the reaction. Similarly, internal donor is also an important component in further improving the activity and stability of active sites.

The preparation of a high-efficiency magnesium chloride supported vanadium/titanium bimetallic Ziegler-Natta catalyst with di-*i*-butyl phthalate (DIBP) as internal donor, and its applications in copolymerization of ethylene and propylene using triethylaluminium (AlEt₃) as the co-catalyst are reported in this article. The effects of reaction conditions such as polymerization temperature, ethylene/propylene molar ratio and Al/V molar ratio on the properties of the catalyst and product were investigated. The comparative study of bimetallic catalyst with single metallic catalysts on the catalytic activity and the properties of the obtained products were carried out.

EXPERIMENTAL

All operations were carried out under high pure nitrogen atmosphere using standard Schlenk techniques.

Materials

Polymerization-grade ethylene, propylene and high pure nitrogen, supplied by Daqing Petrochemical Co., Ltd., were used after passage through 0.4 nm molecular sieve (Fluka Chemical Corp., Buchs, Switzerland). Triethylaluminium (AlEt₃; Ethyl Co., Houston, Texas; 95% purity) was used without further purification. Vanadium tetrachloride (VCl₄), titanium tetrachloride (TiCl₄), DIBP, *n*-hexane and anhydrous magnesium chloride (MgCl₂) were obtained from Beijing Chemistry reagents Co., Ltd. (Beijing, China). MgCl₂·2.56C₂H₅OH complex was prepared according to methods described in the literature^[9].

Preparation of Catalyst

The bimetallic catalytic system was prepared as follows: VCl₄ and TiCl₄ were premixed in a preset vanadium/titanium (V/Ti) molar ratio; excess mixture was injected into a dried Schlenk reactor under the protection of nitrogen and cooled to –20°C. Then, a given amount of MgCl₂·2.56C₂H₅OH complex was added, the temperature was increased to 60°C. Subsequently, the internal donor DIBP was added to the reactor maintaining MgCl₂/DIBP molar ratio of 10:1. The temperature was increased to 110°C within 2 h, then it was held for another 2 h, and the solid components were separated by filtration. For a better immobilization of active sites on MgCl₂ carrier, excess VCl₄ and TiCl₄ mixture was injected into the dried Schlenk reactor again, the temperature was raised and 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 (VCl₄/TiCl₄/MgCl₂/DIBP) was dried in vacuo. The V and Ti contents of the bimetallic catalyst were determined by UV-1700 spectrophotometer (Shimadzu Co., Tokyo, Japan) using the wavelength 450 nm and 410 nm, respectively.

The single metallic vanadium and titanium catalysts were prepared in a similar procedure aforementioned without mixing TiCl₄ and VCl₄, respectively. $\alpha(V) = 5.05$ wt% for VCl₄/MgCl₂/DIBP system and $\alpha(Ti) = 2.02$ wt% for TiCl₄/MgCl₂/DIBP system.

Polymerization

Ethylene and propylene were premixed in a cylinder at the desired molar ratios. Polymerization was carried out in a 250 mL glass reactor equipped with a mechanical stirrer and a temperature control. The reactor was purged three times with highly pure nitrogen. *n*-Hexane as a solvent (100 mL) was saturated with the ethylene-propylene gas mixture at a regulated temperature (controlled by a DF-101S heat-collected constant temperature stirrer, Jiangsu Zhengji Instrumental Co., Ltd, 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. The reaction was stopped after 30 min through the addition of an acidic methanol solution. The products were subsequently filtered off and washed with methanol, and then dried in vacuo at 60°C for 12 h.

Characterization of Products

The weight-average molecular weight (M_w) and molecular weight distribution (MWD) of EP copolymers were measured by a Waters Alliance (Freehold, New Jersey) GPCV-2000 equipped with a refractive-index detector with three Polymer Laboratory (Amherst, Massachusetts) mixed-B columns. The number-average molecular weight (M_n) and M_w were determined with polystyrene standard calibration as a reference. The following operating conditions were used: (1) solvent: 1,2,4-trichlorobenzene, flow rate: 1.0 mL min⁻¹; (2) antioxidant: 2,6-di-*tert*-butyl-4-methylphenol at a concentration of 1.0 g L⁻¹ as a stabilizer in 1,2,4-trichlorobenzene; (3) concentration of samples: 1 g L⁻¹ (dissolution of the sample in stabilized 1,2,4-trichlorobenzene was carried out by heating at 150°C for 24 h with gentle agitation); (4) injection volume: 200 µL; (5) testing temperature: 150°C.

The melting temperature and enthalpy of fusion of EP copolymers were measured by a Perkin-Elmer (Waltham, Massachusetts) DSC-7 differential scanning calorimeter in the following way. The sample (6–7 mg) was heated to 210°C at 10 K min⁻¹ and held for 5 min to remove the thermal history. Then, it was cooled to 50°C at 10 K min⁻¹, and this was followed by reheating at 10 K min⁻¹. The DSC curve of each sample was recorded in the second heating run.

¹³C-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

In addition to the catalytic systems used, the properties of an EP copolymer significantly depends on polymerization conditions such as temperature, ethylene/propylene (E/P) molar ratio, cocatalyst and its loading *etc*^[10].

The Effects of Polymerization Reaction Temperature

The effect of polymerization temperature on the catalytic activity is shown in Table 1. According to previous reports^[11, 12], the copolymerization of ethylene and propylene was carried out using the bimetallic catalyst at temperatures ranging from 0°C to 40°C. The increased temperature in the range studied caused a decrease in catalytic activity. This may be attributed to two reasons: on the one hand, the decay rate constants and the thermo-sensitivity of active sites both increase at higher temperatures, which leads to the catalytic activity decreasing at some extend; on the other hand, the solubility of the monomers in *n*-hexane declines at higher temperatures, which leads to a decline in concentration of the monomers around the active sites. Higher efficiency of this bimetallic catalyst was obtained at low temperatures.

Table 1. The effects of the polymerization temperature on the catalytic activity

Temperature (°C)	Activity (g EPR·(gcat) ⁻¹ ·h ⁻¹)
0	161.7
10	145.8
20	125.4
30	124.1
40	108.2

Polymerization conditions: catalyst loading = 0.1 g, E/P molar ratio = 44/56, Al/V molar ratio = 246, solvents = *n*-hexane, polymerization time = 30 min

The Effects of Ethylene/Propylene Molar Ratio

The effects of ethylene/propylene molar ratios on the catalytic activity are listed in Table 2. Copolymerization was carried out at 20°C for better control of the reactions. The E/P molar ratio varied from 10/90 to 80/20 in the polymerization process. With an increase in the E/P molar ratio, the activity increases initially and reaches a peak at E/P molar ratio = 60/40. The high catalytic activity may be attributed to the excellent synergistic effects of the two monomers as reported by Kravchenko *et al.*^[13]. They claimed that the increased rate could not be explained by the greater rate of ethylene (or propylene) insertion, but was likely the result of the activation of dormant catalyst sites by ethylene (or propylene).

Table 2. The effects of the E/P molar ratio on the catalytic activity

E/P molar ratio	Activity (g EPR·(gcat) ⁻¹ ·h ⁻¹)
10/90	122.6
30/70	124.0
60/40	132.5
70/30	122.4
80/20	108.9

Polymerization conditions: catalyst loading = 0.1 g, temperature = 20°C,
Al/V molar ratio = 246, solvent = *n*-hexane, polymerization time = 30 min

The Effects of Al/V Molar Ratio

As a cocatalyst, AlEt₃ has an important effect on catalytic activity^[14]. The effects of the Al/V molar ratios on the catalytic activity are given in Table 3. In this study, the activity increases with increasing Al/V molar ratio at lower ratios but the activity levels off at higher ratios. There are two functions of the cocatalyst AlEt₃: (1) AlEt₃ reduces the contaminants in the polymerization medium, and (2) the active sites are formed by the interaction of AlEt₃ with TiCl₄ or VCl₄. With the increase of the amount of AlEt₃, more vanadium and titanium species are activated and then increase the catalytic activity. However, the increase in catalytic activity is not apparent when the Al/V molar ratio is higher than 345. At a high concentration of AlEt₃, high-valence active centres were over-reduced to low-valence centres, which are active only for ethylene polymerization^[15].

Table 3. The effects of the Al/V molar ratio on the catalytic activity

Al/V molar ratio	Polymer yield (g)	Activity (g EPR·(gcat) ⁻¹ ·h ⁻¹)
49	4.60	92.0
98	5.27	105.4
246	6.27	125.4
345	6.55	131.0
492	6.58	131.6

Polymerization conditions: catalyst loading = 0.1 g, temperature = 20°C, E/P molar ratio = 44/56,
solvent = *n*-hexane, polymerization time = 30 min

The Effects of Ti/V Molar Ratio

The catalytic activity and the composition of products obtained from catalyst with different Ti/V molar ratio are given in Table 4. For copolymerization catalyzed by single metallic catalysts, titanium-based catalyst exhibited high activity but low propylene content in the copolymer, while vanadium-based catalyst produced copolymer with higher propylene content at the cost of activity. Both high catalytic activity and high propylene content were obtained simultaneously when the bimetallic catalyst was employed.

Besides, from the composition of the products, it can be found that the bimetallic catalyst showed higher selectivity for propylene than the two single metallic catalysts. This indicated that interaction between Ti and V had occurred. The research in detail is underway.

From our previous research^[16], internal donor plays an important role in improving the activity of MgCl₂-supported vanadium-based catalysts. The function of DIBP in MgCl₂-supported catalysts is twofold:

(1) stabilizing small primary crystallites of magnesium chloride, and (2) controlling the amount and distribution of transition metal compounds in the final catalyst^[17]. Thus, a possible reason for higher productivity of DIBP catalysts is that bidentate dialkylphthalate is bound to the adjacent MgCl₂ layers on (110) lateral cuts, and is able to hold the layers during polymerization. This may stabilize the MgCl₂ crystallites, hence the active sites of this bimetallic catalyst are stable. Several physical and chemical processes will occur during polymerization, leading to substantially high productivity of phthalate catalysts^[18].

Table 4. The effects of the Ti/V molar ratio on the catalytic activity

Catalyst	V/Ti (molar ratio)	Activity (g EPR·(gcat) ⁻¹ ·h ⁻¹)	Sequential composition (mol%)	
			P	E
VCl ₄ /MgCl ₂ /DIBP	10/0	22.4	32.1	67.9
VCl ₄ /TiCl ₄ /MgCl ₂ /DIBP	7/1.8	87.5	44.7	55.3
VCl ₄ /TiCl ₄ /MgCl ₂ /DIBP	4/3.4	105.4	56.0	44.0
VCl ₄ /TiCl ₄ /MgCl ₂ /DIBP	2/3.8	110.6	26.8	63.2
TiCl ₄ /MgCl ₂ /DIBP	0/4.2	116.8	21.9	78.1

Polymerization conditions: catalyst loading = 0.1 g, temperature = 20°C, Al/V molar ratio = 98, Al/Ti molar ratio = 90, E/P molar ratio = 44/56, solvent = *n*-hexane; polymerization time = 30 min

¹³C-NMR Analysis

¹³C-NMR analysis was carried out to characterize the composition of the EP copolymers. All the resonance peaks were assigned using the terminology used by Carman and Wilkes^[19]. The composition and the sequence distribution can be estimated from the spectra according to the calculation scheme proposed by Randall^[20]. The monomer reactivity ratios, r_E and r_P (E = ethylene, P = propylene) are based on dyads using the following equations^[21]:

$$r_E = \frac{[P]_0}{[E]_0} \times \frac{2[EE]}{[EP]} \quad (1)$$

$$r_P = \frac{[E]_0}{[P]_0} \times \frac{2[PP]}{[EP]} \quad (2)$$

$$r_E r_P = \frac{4[EE][PP]}{[EP]^2} \quad (3)$$

where ([EE], [EP], [PP]) and ([E]₀, [P]₀) denote dyad sequence distributions in the copolymers and the initial monomer concentrations in liquid phase. The concentration ratios under the reaction conditions were calculated by the equation quoted by Ferreira *et al*^[22]. Results are given in Table 5.

The catalyst produced a copolymer with high propylene content (56.04 mol%). It means that the catalyst could make the insertion of propylene into the copolymer chains more effectively. Monomer reactivity ratios can be used to access the “character” of the copolymerization. When $r_E r_P > 1$, the copolymer has a blocked character. When $r_E r_P \approx 0$, the polymerization has an alternating character. When $r_E r_P = 1$, the polymerization is random in character^[23]. The $r_E r_P$ value ($r_E r_P = 1.919$) suggests that this bimetallic catalyst gives random or short blocked copolymer. Besides, the r_P value was found to be very low, which also indicates that this catalytic system favors copolymerization of ethylene and propylene. Because of the high propylene content in the copolymer, the structure and properties of the copolymer were mainly determined by the sequences of polypropylene fragments.

Table 5. ^{13}C -NMR analysis of copolymer obtained by $\text{VCl}_4/\text{TiCl}_4/\text{MgCl}_2/\text{DIBP}$ catalyst

Sequences distributions		Composition
Monad distribution (mol%)	[E]	43.96
	[P]	56.04
Dyad distribution (mol%) ^a	[EE]	24.06
	[EP]	41.54
	[PP]	34.40
Triad distribution (mol%)	[EEE]	13.27
	[PEE]	21.58
	[EPE]	7.884
	[PPP]	20.65
	[PPE]	27.51
	[PEP]	9.106
Reactivity ratio	r_{E}	5.909
	r_{P}	0.325
	$r_{\text{E}}/r_{\text{P}}$	1.919

Polymerization conditions: E/P molar ratio = 44/56, Al/V molar ratio = 98, temperature = 20°C;

P = propylene, E = ethylene; r_{E} = reactivity ratio for ethylene, r_{P} = reactivity ratio for propylene;

^a [EE] = [EEE] + 1/2[PEE], [EP] = [PEP] + [EPE] + 1/2([PEE] + [PPE]), [PP] = [PPP] + 1/2[PPE]

Gel Permeation Chromatography

The molecular weight and molecular weight distribution of copolymers can be controlled by a variety of tailoring methods^[24], among which designing a good catalytic system is an effort-saving one. The properties of copolymers produced by supported bimetallic catalyst were assessed by investigating the M_{w} and MWD of copolymers with different E/P molar ratios. The results are illustrated in Table 6.

Table 6. Gel permeation chromatography results for copolymers with different E/P molar ratios

E/P molar ratio	$M_{\text{n}} \times 10^{-3}$	$M_{\text{w}} \times 10^{-5}$	MWD
10/90	9.7	1.8	18.3
30/70	4.1	1.5	35.4
44/56	4.4	1.7	39.0
60/40	4.8	2.6	54.5
70/30	6.1	5.0	81.5
80/20	8.0	4.9	60.9

Polymerization conditions: Al/V molar ratio = 246, temperature = 20°C, polymerization time = 30 min

The copolymers had a high molecular weight and a broad MWD. The high activation energies of the chain-transfer and chain-deactivation reactions relative to the chain-propagation reaction lead to the high molecular weight^[25]. With the increase of E/P molar ratio, M_{w} and MWD value increased accordingly. This may be explained that the molecular weight of polyethylene is usually higher than that of polypropylene synthesized by the same catalyst. The relatively higher molecular weight of the copolymer (E/P molar ratio = 10/90) is hard to understand. This also implied that the M_{w} value is dependent on the comonomer content. The heterogeneity of supported bimetallic Ziegler-Natta catalysts is responsible for the broad MWD of the copolymers. Since EP copolymers with the broad MWD usually have excellent processability, it is reasonable to expect their wide application areas.

Differential Scanning Calorimetry

The melting temperature and crystallinity (X_{c}) of the products as a function of the E/P molar ratio are evaluated in Table 7. The melting temperature is about 115–120°C, which is within the range of the ethylene sequences (60–135°C)^[26]. The crystallinity of the copolymer samples was calculated using methods described

previously^[27]. The lowest X_c value is obtained at the E/P molar ratio of 44/56, but copolymers prepared at either higher ethylene content or propylene content has higher X_c value. Herein, the copolymers produced by this bimetallic catalyst are almost amorphous (X_c is below 20%). Shin *et al.*^[28] has reported that random EP copolymers demonstrated minimal crystallinity.

Table 7. Differential scanning calorimetry results for copolymers with different E/P molar ratios

E/P molar ratio	T_m (°C)	ΔH_f (J/g)	X_c (%)
10/90	139.9	47.5	16.4
30/70	116.5	32.6	11.3
44/56	115.9	16.5	5.7
60/40	117.5	20.0	6.9
70/30	118.2	35.0	12.1
80/20	119.9	58.8	20.3

Polymerization conditions: Al/V molar ratio = 246, temperature = 20°C, polymerization time = 30 min; ΔH_f = enthalpy of fusion; T_m = melting temperature; X_c = crystallinity

In the current research, the behavior of the copolymers with low comonomer content and the corresponding homopolymer is similar. The copolymer (from E/P molar ratio = 10/90) showed a melting temperature of 140°C. Since the highest melting temperature of polyethylene is about 135°C, the copolymer with the melting temperature above 135°C could be ascribed to polypropylene fragments. For propylene sequences, the melting temperatures usually fall in the range of 120–160°C^[29]. Therefore, we can conclude that this copolymer contains high propylene content. Owing to the limitation in the length of propylene sequences, this copolymer had a lower melting temperature than propylene homopolymer.

CONCLUSIONS

MgCl₂-supported vanadium/titanium bimetallic Ziegler-Natta catalysts with DIBP as internal donor were prepared and applied in the copolymerization of ethylene and propylene with AlEt₃ as the co-catalyst. A much higher activity was obtained compared to that of the traditional single metallic vanadium catalyst. Meanwhile, the propylene content in the EP copolymer produced by this bimetallic catalyst is higher than that of the copolymer obtained by single titanium catalyst. By employing the bimetallic catalyst, random or short blocky type of EP copolymers with high propylene content were obtained, which were found to have broad molecular weight distribution, low melting temperature and low crystallinity.

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