

Comonomer Effects in Copolymerization of Ethylene and 1-Hexene with MgCl₂-Supported Ziegler-Natta Catalysts: New Evidences from Active Center Concentration and Molecular Weight Distribution

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ABSTRACT: In this article, comonomer effects in copolymerization of ethylene and 1-hexene with four MgCl₂-supported Ziegler-Natta catalysts using either ethylene or 1-hexene as the main monomer were investigated. It was found that no matter which monomer was used as the main monomer, the polymerization activity was significantly enhanced by introducing small amount of comonomer. In copolymerization with ethylene as the main monomer, the strength of comonomer effects was much stronger in active centers producing low-molecular-weight polymer than those producing high-molecular-weight polymer. In copolymerization with 1-hexene as the main monomer, the number of active centers ($[C^*]/[Ti]$) was determined, and the propagation rate constants (k_p) were calculated. Deconvolution of the polymer molecular weight distribution into Flory components were made to study the active center distribution. Introduction of small amount of ethylene caused marked increase in the number of active centers and decrease in average chain propagation rate constant. Introducing internal electron donor in the catalyst enhanced not only the number of active centers but also the chain propagation rate constant. In copolymerization of 1-hexene with small amount of ethylene, the internal donor weakened the comonomer effects to some extent and changed the distribution of comonomer effects among different types of active centers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41264.

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INTRODUCTION

Linear low-density polyethylene (LLDPE) is a copolymer of ethylene and C₄–C₈ α -olefins. Because it contains a small amount of short-chain branches along the backbone of polymer chain, its crystallinity, melting temperature, and density are lower than ethylene homopolymer. These structural features make LLDPE a suitable material in the application fields like films and cables. More than 30 million tons of LLDPE resin is now produced every year in the world. Because of its great importance, many literatures have been published in the studies of ethylene/ α -olefin copolymerization catalyzed by supported Ziegler-Natta catalysts and metallocene catalysts.^{1–11} More than 80% of LLDPE production has been performed by supported Ziegler-Natta catalysts because of their low cost and high performance.^{12,13} Because the properties of LLDPE depend largely on the amount of incorporated α -olefin, many literatures investigated the effects of catalyst structure, type of cocatalyst as well as comonomer

concentration on the comonomer incorporation rate.^{14–19} As an important feature, Ziegler-Natta catalysts produce ethylene- α -olefin copolymer with broad chemical composition distribution (CCD), which is a result of multiple active centers on the catalyst, and the α -olefin units are highly enriched in the part of polymer with low molecular weight.^{7,11,12,20–23} Such broad CCD significantly influences the application properties of the copolymer.

In ethylene/ α -olefin copolymerization with heterogeneous Ziegler-Natta catalysts, strong enhancement of reaction activity by the α -olefin (so-called “comonomer effect”) has long been reported and studied, but its mechanism is still not confirmed.^{7,11,24–28} On the other hand, activation of α -olefin polymerization by ethylene in heterogeneous Ziegler-Natta catalysis systems has also been reported in many literatures.^{29–34} It can be considered as another type of comonomer effect. This activation effect has been explained as releasing of Ti—CH(CH₃)—

Polymer type dormant active centers by insertion of an ethylene.^{29–32} In our previous work, 1-hexene homopolymerization and 1-hexene/ethylene copolymerization with $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(\text{C}_2\text{H}_5)_3$ catalyst were compared to investigate the effect of ethylene on the distribution of active centers.³⁴ Adding small amount of ethylene in 1-hexene polymerization markedly increased the number of active centers that produce low-molecular-weight polymer. This phenomenon agrees with the mechanism suggesting the presence of $\text{Ti-CH}(\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$ type dormant sites and their activation by ethylene.

In this article, the above-mentioned two types of comonomer effects in copolymerization of ethylene and 1-hexene with MgCl_2 -supported Ziegler-Natta catalysts have been investigated, with attention being paid to the effects of comonomer on the distribution and intrinsic activity of the multiple types of active centers. A method using cinnamoyl chloride as quenching reagent has been adopted for counting the active centers.^{34,35} The results obtained in this work form new evidences for understanding the mechanism of the comonomer effects and may provide clues for figuring out structure of different types of active centers.

EXPERIMENTAL

Materials

The simple $\text{TiCl}_4/\text{MgCl}_2$ type supported Ziegler-Natta catalyst (Cat-1) was prepared through reaction of $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct with TiCl_4 . Two $\text{TiCl}_4/\text{Di}/\text{MgCl}_2$ type supported Ziegler-Natta catalysts containing internal electron donor (Di) were prepared through reaction of $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct with TiCl_4 in the presence of phthalic anhydride and anisole, respectively. The catalyst containing diethylphthalate as Di is named as Cat-2, and that containing anisole is named as Cat-3. The preparation procedures and characterization of these catalysts have been described in a previous work.³⁶ Ti contents of Cat-1, Cat-2, and Cat-3 determined by spectrophotometry method are 8.2, 4.4, and 9.2%, respectively. Cat-1 was used for ethylene/1-hexene copolymerization where ethylene was the main monomer. For copolymerization experiments where 1-hexene was the main monomer, Cat-1, Cat-2, Cat-3, and a commercial Ziegler-Natta catalyst DQ ($\text{MgCl}_2/\text{dibutylphthalate}/\text{TiCl}_4$, produced by SINOPEC) with a Ti content of 2.7 wt % were used. 1-Hexene (98%) and *n*-heptane (solvent) were purchased from Acros Organics and purified by refluxing over metal Na for 6 h and distilled before use. Ethylene (polymerization grade product of SINOPEC Shanghai Petrochemical Co.) was further purified by passing through a column filled with deoxygen reagent and molecular sieves. $\text{Al}(\text{C}_2\text{H}_5)_3$ (TEA) was purchased from Almarle Co. and diluted in *n*-heptane to 1M before use. Cinnamoyl chloride (98%) was purchased from Alfa Aesar Co. and diluted with *n*-heptane to 1 M before use.

Polymerization and Quenching Reaction

All of the polymerizations were performed in a 500-mL Schlenk flask equipped with magnetic stirrer under the protection of pure nitrogen (99.999%). In the copolymerization runs with ethylene as the main monomer, the flask was first evacuated and filled with 1 atm nitrogen and immersed in a 40°C oil bath during the reaction. The reagents were added in the order of

solvent, 1-hexene, AlEt_3 ($\text{Al}/\text{Ti} = 50$). Ethylene at 1.1 bar pressure was bubbled through the solution under stirring for 10 min, and then about 30 mg of Cat-1 was added to start the polymerization. The reaction was terminated by small amount of ethanol after 8 min; during this period, ethylene gas was continuously supplied to the reactor. In the copolymerization runs with 1-hexene as the main monomer, the flask filled with 1 atm nitrogen was connected to a metal cylinder containing nitrogen/ethylene mixture with nitrogen partial pressure of 1 atm and ethylene partial pressure ranging from 0.05 to 0.4 atm. By continuously bubbling the nitrogen/ethylene mixture through the reaction solution, ethylene partial pressure in the reactor was maintained at 0.05, 0.1, 0.2, or 0.4 atm, respectively. Reagents were added in the order of solvent, 1-hexene, AlEt_3 ($\text{Al}/\text{Ti} = 50$), and the catalyst. The total volume of liquid phase in the polymerization runs was 300 mL. The initial [1-Hexene] was 1 mol/L. After 6 min of polymerization at 40°C using DQ or 8 min of polymerization at 70°C using Cat-1, Cat-2, or Cat-3, cinnamoyl chloride (cinnamoyl chloride/Al (molar ratio) = 3 : 1) was injected into the reactor to quench the polymerization.³⁵ After 10 min of quenching reaction, isopropyl alcohol/hydrochloric acid (200 : 1, v/v) mixture was added to decompose the catalyst, cocatalyst, and unreacted cinnamoyl chloride, and the polymer was precipitated with excess of isopropyl alcohol. The polymer after thorough purification was dried in vacuum at 60°C.

The content of carbonyl in the quenched polymers was determined spectrophotometrically with a Varian Cary 100 Bio UV-Vis spectrometer as reported in our previous work.³⁵ It has been proved that each propagation chain existing in the system at the time of quenching is labeled with a carbonyl group after the reaction with cinnamoyl chloride, thus the number of carbonyl corresponds to the number of active centers.

Polymer Characterization

The molecular weight and molecular weight distribution (MWD) of the polymer samples were measured by gel permeation chromatography (GPC) in a PL 220 GPC instrument (Polymer Laboratories). For polyethylene and copolymers of low 1-hexene content, 1,2,4-trichlorobenzene was the solvent and the column temperature was 150°C. For poly(1-hexene) and copolymers containing small amount of ethylene, the measurement was conducted at 30°C in tetrahydrofuran. Three PL mixed B columns ($500 - 1 \times 10^7$) were used. Universal calibration against narrow polystyrene standards was adopted.

RESULTS AND DISCUSSION

Effects of Small Amount of 1-Hexene on Ethylene Polymerization

The results of ethylene homopolymerization and ethylene/1-hexene copolymerization (ethylene was the main monomer) catalyzed by a simple $\text{TiCl}_4/\text{MgCl}_2$ type Ziegler-Natta catalyst (Cat-1) were summarized in Figure 1. Obviously, introduction of small amount of 1-hexene markedly enhanced the catalytic activity, but reduced the molecular weight of the resultant copolymers. In the MWD curves of the polymer samples, simultaneous shifting toward low-molecular-weight and broadening

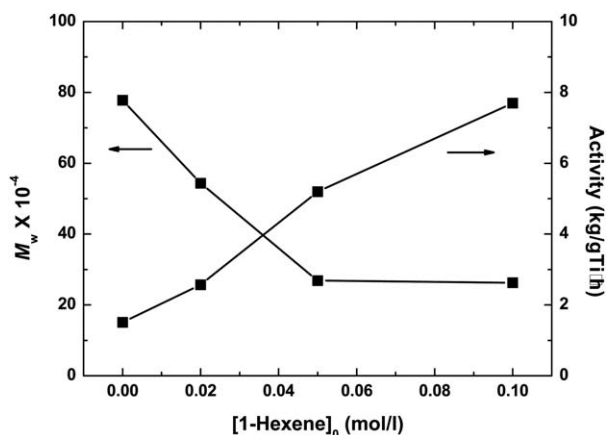


Figure 1. Influence of $[1\text{-Hexene}]_0$ on the polymerization activity of ethylene/1-hexene copolymerization and molecular weight of the copolymer. Conditions of polymerization: $T_p = 40^\circ\text{C}$, $Al/Ti = 50$, $P_E = 1.1$ atm, time = 8 min.

of the MWD peak with increasing $[1\text{-Hexene}]_0$ can be clearly seen (see Figure 2).

To study the effects of comonomer on the active center distribution (ACD), deconvolution of the polymer's MWD curves with several Schulz-Flory most-probable distributions has been applied. This kind of deconvolution treatment has been proved useful and reliable for differentiating the different active sites in heterogeneous Ziegler-Natta catalysts.^{7,37-43} The MWD curves of the polymer samples in Figure 2 were satisfactorily deconvoluted into five Flory components, respectively, and these components were named as component I, II, III, IV, and V in the order of decreasing molecular weight. Each Flory component can be ascribed to polymer produced by a certain type of active center.^{7,37-43} Thus, five types of active centers, C_I^* , C_{II}^* , C_{III}^* , C_{IV}^* , and C_V^* can be distinguished. Among them C_I^* produces polymer with the highest molecular weight and C_V^* produces polymer with the lowest molecular weight. The results of MWD deconvolution, namely, the weight fraction and weight average molecular weight of each Flory component, are summarized in Table I. By multiplying the fraction of the component by the total activity of polymerization, the polymerization activity of each type of active center has also been calculated.

As shown in Table I, introduction of 1-hexene resulted in decrease in the weight fraction of components I and II but increase in the weight fraction of components IV and V. However, the weight fraction of components III did not change much. Interestingly, the catalytic activity of all the five active center types increased in the presence of 1-hexene as shown in Figure 3. The activity increment of active centers C_{III}^* , C_{IV}^* , and C_V^* was much larger than that of C_I^* and C_{II}^* . For example, the activity of C_V^* was increased more than 15 times when $[1\text{-Hexene}]_0$ was increased from 0 to 0.1 mol/l, but the activity of C_I^* was only doubled after than same change of $[1\text{-Hexene}]_0$. Such differentiation of comonomer effects among different active centers can be a solid evidence for the chemical-based explanation to comonomer effects, although diffusion barrier in the polymerization system may still play a partial role. It indicated that

the influence of 1-hexene concentration on the catalytic activity of C_{III}^* , C_{IV}^* , and C_V^* was more significant than that of C_I^* and C_{II}^* . Namely, the introduction of 1-hexene activated those active centers producing low-molecular-weight polymer more efficiently than those producing high-molecular-weight polymer, leading to significant decrease in average molecular weight of the whole polymer and broadening of its MWD. Similar phenomena have been reported by Kissin et al., although at much higher temperature and comonomer concentration.^{7,41} According to Kissin's research, the ability to copolymerize α -olefins with ethylene steadily decreases from C_V^* to C_I^* and C_{II}^* . That is to say, those active centers producing low-molecular-weight polymer have better copolymerization ability. When a small amount of 1-hexene was introduced into polymerization system, the catalytic activity of those active centers which were more sensitive to 1-hexene showed a larger increase. This confirmed the experimental result above that the introduction of 1-hexene activated those active centers producing low-molecular-weight polymer more efficiently. Table I shows that the molecular weight of each Flory component was also decreased after the introduction of 1-hexene, but its influence on the molecular weight of the whole polymer is less important.

According to a mechanism model proposed by Kissin et al.,⁷ the comonomer effects in ethylene/1-hexene copolymerization can be explained by the activation effect of 1-hexene as shown in Scheme 1. In this model, the $Ti-C_2H_5$ species that are formed by alkylation of the supported $TiCl_x$ species or by insertion of ethylene in $Ti-H$ have high probability to enter a dormant state where the vacancy of Ti is occupied by H from the methyl group for strong β -agostic interactions. This will cause severe depression of the catalytic activity, because many Ti species now become actually inactive. When α -olefin was introduced into the system, its insertion into the $Ti-H$ bond leads to $Ti-C_6H_{11}$ species that are not dormant. Consequently, a large portion of dormant species can be released, leading to significantly enhanced activity in the copolymerization system. Our experimental results indicated that those active centers producing low-molecular-weight polymers were more prone to form dormant centers compared with active centers producing high-molecular-weight polymers. As a result, those newly emerging active centers were mainly active centers producing low-molecular-weight polymers.

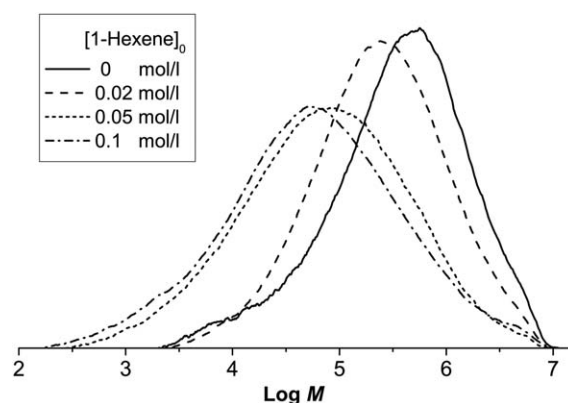


Figure 2. MWD curves of ethylene/1-hexene copolymers.

Table I. Results of MWD Curve Deconvolution

Entry	[1-Hexene] ₀ (mol/l)	M _w (10 ⁴)	Component	M _w (10 ⁴)	Fraction (%)	Activity (Kg/gTi·h)
1	0	77.8	I	241.0	19.0	0.29
			II	69.7	39.8	0.60
			III	24.3	27.1	0.41
			IV	6.4	10.1	0.15
			V	1.2	4.0	0.06
2	0.02	54.3	I	227.3	12.2	0.31
			II	68.5	27.1	0.70
			III	25.6	32.6	0.84
			IV	9.5	21.7	0.56
			V	2.7	6.5	0.17
3	0.05	26.8	I	152.7	8.4	0.44
			II	39.2	23.8	1.24
			III	11.1	31.0	1.61
			IV	3.2	25.1	1.30
			V	0.8	11.7	0.61
4	0.1	26.3	I	188.7	7.6	0.58
			II	39.9	20.1	1.55
			III	10.6	30.2	2.33
			IV	3.1	28.6	2.21
			V	0.8	13.4	1.03

Effects of Small Amount of Ethylene on 1-Hexene Polymerization

In industrial production of propylene/ethylene copolymer that contains small amount of ethylene (usually less than 5 mol %), usually a TiCl₄/internal donor/MgCl₂ type catalyst is used.⁴⁴ In this section, an industry catalyst named DQ that contains dibutylphthalate as internal donor was used for 1-hexene/ethylene copolymerization, with an aim to imitate the propylene/ethylene copolymerization system. The number of active centers ([C*]/[Ti]) in the polymerization systems was determined by a quenching method reported in our previous work, and the aver-

age chain propagation rate constant was calculated using the data of [C*] and polymerization activity.³⁵ As shown in Table II, introducing small amount of ethylene caused moderate increase of activity, which was the combined effects of evident increase in [C*] and decrease in the *k_p* value. These changes continued as the ethylene concentration was further increased. This phenomenon is basically the same as that reported in our previous work.³⁴

The MWD curves of the first four samples in Table II were also satisfactorily deconvoluted into five Flory components, respectively, and these components were named as component A, B, C, D, and E, in the order of decreasing molecular weight. As shown in Table III, introduction of ethylene resulted in slight decrease in the weight fraction of components A and B, and slight increase in the weight fraction of components D and E. Weight fraction of component C was less affected. Furthermore, as shown in Figure 4, increase in partial pressure of ethylene caused almost no changes in the catalytic activity of C_A^{*} and C_B^{*}, but those of C_C^{*}, C_D^{*}, and C_E^{*} were obviously increased. It also indicated that the comonomer effect of ethylene in an α -olefin

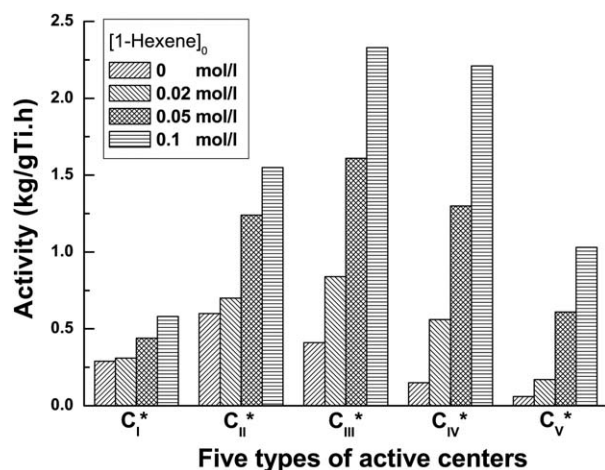
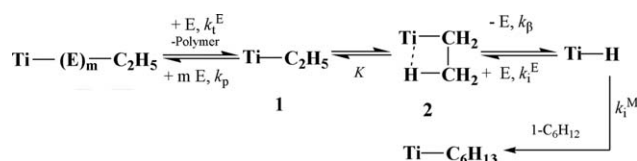


Figure 3. Influence of [1-Hexene]₀ on the activity of five active center types in TiCl₄/MgCl₂ catalyst.



Scheme 1. Proposed kinetic mechanism of ethylene/1-hexene copolymerization.

Table II. Effects of Ethylene on $[C^*]$ and k_p in 1-Hexene Polymerization Catalyzed by DQ Catalyst

Entry	P_{Ethylene} (atm)	Activity (Kg/gTi·h)	M_w (10^5)	PDI	$[C^*]/[Ti] \times 10^3$ (mol/mol)	k_p (L/mol·s)
5	0	10.1	7.42	10.6	12.9	221
6	0.05	11.0	5.45	11.6	31.9	93.6
7	0.1	12.0	5.58	11.4	41.9	77.9
8	0.2	13.1	3.52	7.9	96.5	36.9
9	0.4	14.3	3.36	9.0	135	30.1

Polymerization conditions: Cocatalyst: TEA; Al/Ti = 50; $[1\text{-Hexene}]_0 = 1 \text{ mol/l}$; $T_p = 40^\circ\text{C}$; time = 6 min.

polymerization system is to selectively activate the active centers producing low-molecular-weight polymer.

As reported in the previous work,³⁴ increase of $[C^*]$ by small amount of ethylene can be largely attributed to activation of dormant centers that have rather low k_p values and produce low-molecular-weight polymer. These dormant centers may be formed by 2,1-insertion of 1-hexene in a Ti—H bond, and activated by insertion of an ethylene (see Scheme 2). It has been found that insertion of ethylene in such dormant centers is much faster than that of propylene or other α -olefins.^{29–31}

Influences of Internal Donor on the Comonomer Effects

Comparing Figure 4 with Figure 3, we find that the activation effect of ethylene on 1-hexene polymerization is much weaker than the activation effect of 1-hexene on ethylene polymerization. It means that there could be much more Ti-ethyl type dormant centers than the Ti-hexyl type dormant centers. Another

factor that can affect the strength of comonomer effects could be the presence of internal electron donor, because Di may deactivate some types of active centers, resulting in strong changes of the ACD and the proportion of dormant centers. To clarify the influences of Di on comonomer effects, 1-hexene homopolymerization and 1-hexene/ethylene copolymerization with three catalysts Cat-1, Cat-2, and Cat-3 were conducted under the same conditions. Here, the Cat-1 contains no Di, Cat-2 contains phthalate type Di, and Cat-3 has ether type Di. Each polymerization run has been quenched by cinnamoyl chloride for measuring the active center concentration. The results are listed in Table IV.

It is seen that the catalyst containing anisole (Cat-3) showed the highest activity, but the blank catalyst (Cat-1) was the least active. The strength of the comonomer activation effect (activity ratio of copolymerization/homopolymerization) decreased in the order of Cat-1 > Cat-2 > Cat-3. The number of active

Table III. Results of MWD Curve Deconvolution

Entry	P_{Ethylene} (atm)	M_w (10^4)	PDI	Component	M_w (10^4)	Fraction (%)	Activity (Kg/gTi·h)
5	0	7.42	10.6	A	200.0	10.6	1.07
				B	43.9	23.8	2.41
				C	13.2	29.6	2.99
				D	4.2	26.3	2.65
				E	1.3	9.7	0.98
6	0.05	5.45	11.6	A	188.7	7.8	0.86
				B	38.3	19.5	2.15
				C	10.5	29.4	3.24
				D	3.3	31.6	3.48
				E	1.0	11.7	1.28
7	0.1	5.58	11.4	A	172.4	8.4	1.00
				B	37.7	21.1	2.53
				C	10.4	30.8	3.70
				D	3.2	29.5	3.54
				E	0.9	10.3	1.23
8	0.2	3.52	7.9	A	91.7	8.4	1.10
				B	27.7	19.4	2.54
				C	8.8	30.0	3.93
				D	2.9	29.8	3.90
				E	0.9	12.4	1.62

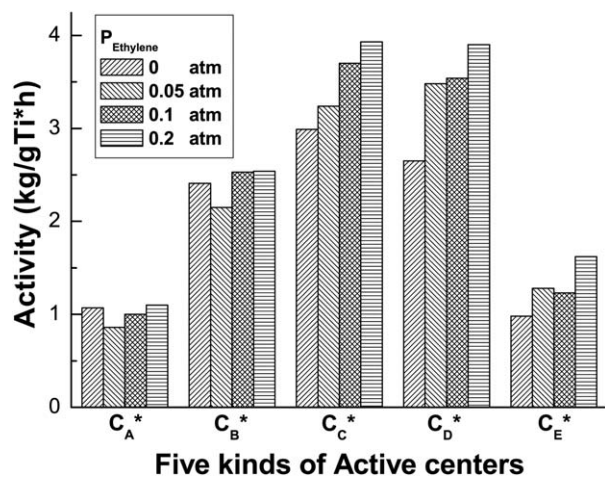


Figure 4. Influence of ethylene pressure on the activity of five types active centers in $\text{TiCl}_4/\text{dibutyl phthalate}/\text{MgCl}_2$ catalyst

centers was markedly increased by introducing Di in the catalysts, especially when anisole was the Di. This means that addition of Di can result in formation of more active species. The most possible reason may be that addition of Di would strongly change the surface structure and specific surface area of the catalyst. In all the three catalysts, the number of active centers increased markedly with addition of small amount of ethylene, and the $[\text{C}^*]$ increment also decreased in the order of $\text{Cat-1} > \text{Cat-2} > \text{Cat-3}$. Cat-3 showed moderate comonomer effects in words of activity and $[\text{C}^*]$ changes. In addition, addition of ethylene caused decrease in the chain propagation rate constant of all the three catalysts, with the decrement decreased in the order of $\text{Cat-2} > \text{Cat-1} > \text{Cat-3}$. If we ignore the increase in k_p value of a part of active centers by ethylene,³⁴ we can estimate the average chain propagation rate constant (k_p') of those active centers that have been activated by ethylene in the copolymerization systems. As shown in the last column of Table IV, adding anisole as Di did not change the intrinsic activity of these newly activated centers, but using phthalate type Di caused evident lowering of k_p' . Using data in Table II, the similarly calculated k_p' value of entry 20 is 10 L/mol·s, which is close to that of Cat-2 . Because both Cat-2 and DQ catalyst contain phthalate type Di, it seems that this kind of bidentate donor can influence the properties of active centers more strongly than monodentate donors like anisole. Because of strong adsorption of phthalate on certain surface locations on the catalyst, intrinsic activity of the centers capable of catalyzing 1-hexene polymerization became higher, as k_p value of Cat-2 is higher than that of Cat-1 in the absence of ethylene. After addition of ethylene, however, the newly activated centers in Cat-2 presented lower activity than those of Cat-1 , possibly for strong coordination of Di to these centers. Judging by these results, we can say that the internal donor does change the strength of comonomer effects by influencing both the number and the intrinsic performances of active centers on the catalyst.

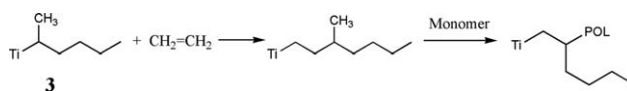
The MWD curves of the six samples in Table IV were deconvoluted into four to five Flory components (component A, B, C, D, and E). Table V shows the weight fractions of the Flory com-

ponents and polymerization activity calculated from these fractions and the total activity of each polymer sample. It is found that the homopolymer and copolymer synthesized with Cat-1 can only be deconvoluted into four Flory components. The molecular weight of component E in these samples may be too low to be collected. The other samples were still satisfactorily deconvoluted into five components.

Similar to the situations in DQ catalyst (see Table III), addition of ethylene caused decreases in molecular weight of the whole polymer and slight decreases in molecular weight of the Flory components. The more important changes are differentiated activation of different components, which can be more clearly seen in Figure 5.

In Figure 5, we can find that the strength of comonomer effect (ratio of the copolymerization activity to the homopolymerization activity) in the four types of active centers of Cat-1 was much stronger than that of the other two catalysts. In Cat-1 , the centers producing high-molecular-weight polymer (C_A^* and C_B^*) experienced stronger activation than the centers producing low-molecular-weight polymer. It has been found that the stereospecificity of active center is roughly proportional to molecular weight of its product.^{34,45–48} Therefore, in the catalyst with no Di, the relatively more stereospecific active centers are more prone to be dormant than the centers with lower stereospecificity. However, with introduction of Di in the catalyst, activation ratios in centers producing low-molecular-weight polymer (C_C^* , C_D^* , and C_E^*) were slightly larger than the centers C_A^* and C_B^* . This may be explained by the roles of Di to further enhance the stereospecificity and regioselectivity of the active centers (it is well known that the stereospecificity and regioselectivity of an active center are directly related³⁰). It is likely that as the regioselectivity of a center exceeds a certain level, probability of 2,1-insertion of α -olefin in Ti-H bond becomes so low to prevent formation of more dormant centers (3) (see Scheme 2), leading to lower activation ratio. When the active center has low stereospecificity and regioselectivity, although facile 2,1-insertion in it may lead to formation of (3), 1,2-insertion of another 1-hexene in the $\text{Ti}-2\text{-hexyl}$ bond may not be so difficult as in the case of active centers with higher stereospecificity, because it has rather open stereochemical environment. Therefore, those active centers with low regioselectivity may slowly recover from the dormant states without the help of ethylene, and thus, they will show weak comonomer effects. Only those active centers with medium stereospecificity and regioselectivity have relatively high tendency to enter the dormant state and need ethylene for activation.

In summary, it seems possible to differentiate the multiple active centers in MgCl_2 -supported Ziegler-Natta catalysts from their comonomer effects. The stereospecificity and regioselectivity of the active centers can be partly probed by measuring the strength of their comonomer effects.



Scheme 2. Activation of Ti -hexyl type dormant center by ethylene.

Table IV. Effects of Ethylene on $[C^*]$ and k_p in 1-Hexene Polymerization Catalyzed by Cat-1, Cat-2, and Cat-3^a

Entry	Catalyst	P_E (atm)	Activity (Kg/g Ti·h)	$[C^*]/[Ti] \times 10^3$ (mol/mol)	C^* load (mmol/g Cat)	k^p (L/mol·s)	k_p^{b} (L/mol·s)
10	Cat-1	0	2.50	8.6	0.015	50	—
11	Cat-1	0.1	4.67	23.6	0.040	38	23
12	Cat-2	0	4.25	11.5	0.011	69	—
13	Cat-2	0.1	6.17	30.0	0.028	30	16
14	Cat-3	0	5.99	22.2	0.043	56	—
15	Cat-3	0.1	7.93	35.2	0.068	48	24

^a Polymerization conditions: Cocatalyst: TEA; Al/Ti = 50; [1-Hexene] = 1 mol/l; T_p = 70°C; time = 8 min.

^b Estimated average chain propagation rate constant of the active centers activated by ethylene.

Table V. Results of MWD Curve Deconvolution

Catalyst	Entry	$P_{Ethylene}$ (atm)	M_w (10^4)	PDI	Component	M_w (10^4)	Fraction (%)	Activity (Kg/gTi·h)
Cat-1	10	0	6.74	3.2	A	45.2	3.8	0.10
					B	14.8	13.5	0.34
					C	5.3	36.7	0.92
					D	1.8	45.9	1.15
					E	—	—	—
Cat-1	11	0.1	5.94	3.6	A	32.4	5.9	0.28
					B	10.3	17.3	0.81
					C	3.9	38.4	1.79
					D	1.3	38.4	1.79
					E	—	—	—
Cat-2	12	0	20.8	8.0	A	194.2	4.7	0.20
					B	50.1	10.8	0.46
					C	14.4	20.6	0.87
					D	4.7	36.1	1.54
					E	1.5	27.9	1.18
Cat-2	13	0.1	9.6	4.9	A	68.5	4.8	0.29
					B	23.7	10.0	0.62
					C	9.4	20.6	1.27
					D	3.7	35.6	2.20
					E	1.3	29.1	1.79
Cat-3	14	0	11.1	6.4	A	72.7	5.5	0.33
					B	16.7	15.0	0.90
					C	5.1	32.8	1.97
					D	1.7	29.9	1.79
					E	0.5	16.8	1.00
Cat-3	15	0.1	8.1	4.7	A	56.2	4.9	0.39
					B	16.8	12.4	0.98
					C	5.9	27.7	2.19
					D	2.6	29.9	2.37
					E	1.0	25.2	2.00

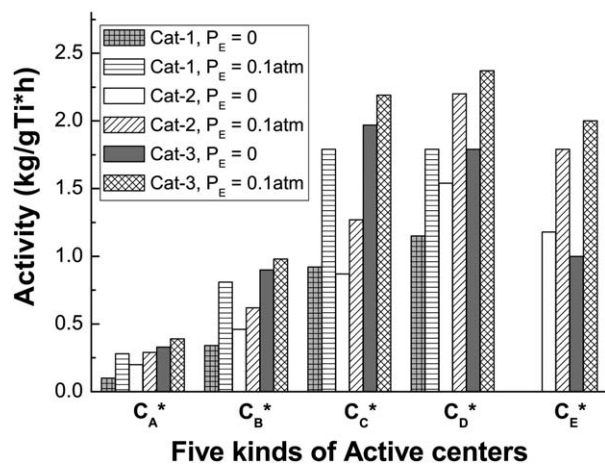


Figure 5. Influence of internal donor on the activity of five types active centers.

CONCLUSION

In copolymerization of ethylene and 1-hexene with $MgCl_2$ -supported Ziegler-Natta catalysts, no matter which monomer was used as main monomer, comonomer effects always exist. The polymerization activity was significantly enhanced by introducing the comonomer. In copolymerization with ethylene as the main monomer, the strength of comonomer effects was much stronger in active centers producing low-molecular-weight polymer than those producing high-molecular-weight polymer. In copolymerization with 1-hexene as the main monomer, introduction of small amount of ethylene caused marked increase in the number of active centers and decrease in average chain propagation rate constant. Introducing internal electron donor in the catalyst not only enhanced the number of active centers but also enhanced the value of propagation rate constant. In copolymerization of 1-hexene with small amount of ethylene, the internal donor weakened the comonomer effects to some extent, and changed the distribution of comonomer effects among the different types of active centers in the catalysis system.

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REFERENCES

- Bialek, M.; Czaja, K. *Polymer* **2000**, *41*, 7899.
- Czaja, K.; Bialek, M. *Polymer* **2001**, *42*, 2289.
- Perin, S. G. M.; Severn, J. R.; Koning, C. E.; Chadwick, J. C. *Macromol. Chem. Phys.* **2006**, *207*, 50.
- Park, H. W.; Chung, J. S.; Baeck, S. H.; Song, I. K. *J. Mol. Catal. A Chem.* **2006**, *255*, 69.
- Cho, H. S.; Choi, D. J.; Lee, W. Y. *J. Appl. Polym. Sci.* **2000**, *78*, 2318.
- Cho, H. S.; Chung, J. S.; Han, J. H.; Ko, Y. G.; Lee, W. Y. *J. Appl. Polym. Sci.* **1998**, *70*, 1707.
- Kissin, Y. V.; Mink, R. I.; Nowlin, T. E. *J. Polym. Sci. A Polym. Chem.* **1999**, *37*, 4255.
- Czaja, K.; Bialek, M.; Utrata, A. *J. Polym. Sci. A Polym. Chem.* **2004**, *42*, 2512.
- Wang, W.; Fan, Z. Q.; Feng, L. X.; Li, C. H. *Eur. Polym. J.* **2005**, *41*, 83.
- Wang, W.; Fan, Z. Q.; Feng, L. X. *Eur. Polym. J.* **2005**, *41*, 2380.
- Chen, Y. P.; Fan, Z. Q. *Eur. Polym. J.* **2006**, *42*, 2441.
- Xia, S. J.; Fu, Z. S.; Huang, B.; Xu, J. T.; Fan, Z. Q. *J. Mol. Catal. A Chem.* **2012**, *355*, 161.
- Kalita, A.; Boruah, M.; Das, D.; Dolui, S. K. *J. Polym. Res.* **2012**, *19*, 1.
- Quijada, R.; Dupont, J.; Lacerda Miranda, M. S.; Scipioni, R. B.; Galland, G. B. *Macromol. Chem. Phys.* **1995**, *196*, 3991.
- Kong, Y.; Yi, J.; Dou, X.; Liu, W.; Huang, Q.; Gao, K.; Yang, W. *Polymer* **2010**, *51*, 3859.
- Senso, N.; Prasertdam, P.; Jongsomjit, B.; Taniike, T.; Terano, M. *Polym. Bull.* **2011**, *67*, 1979.
- Zhang, W. J.; Huang, W.; Liang, T. L.; Sun, W. H. *Chinese J. Polym. Sci.* **2013**, *31*, 601.
- Phiwklaiang, W.; Jongsomjit, B.; Prasertdam, P. *Chinese J. Polym. Sci.* **2014**, *32*, 84.
- Zhang, S. W.; Lu, L. P.; Long, Y. Y.; Li, Y. S. *J. Polym. Sci. A Polym. Chem.* **2013**, *51*, 5298.
- Garoff, T.; Mannonen, L.; Vaananen, M.; Eriksson, V.; Kallio, K.; Waldvogel, P. *J. Appl. Polym. Sci.* **2010**, *115*, 826.
- Nikolaeva, M. I.; Matsko, M. A.; Mikenas, T. B.; Echevskaia, L. G.; Zakharov, V. A. *J. Appl. Polym. Sci.* **2012**, *125*, 2034.
- Nikolaeva, M. I.; Matsko, M. A.; Mikenas, T. B.; Echevskaia, L. G.; Zakharov, V. A. *J. Appl. Polym. Sci.* **2012**, *125*, 2042.
- Lou, J. Q.; Liu, X. Y.; Fu, Z. S.; Wang, Q.; Xu, J. T.; Fan, Z. Q. *Acta Polym. Sinica.* **2009**, *8*, 748.
- Chien, J. C. W.; Nozaki, T. *J. Polym. Sci. A Polym. Chem.* **1993**, *31*, 227.
- Munoz-Escalona, A.; Garcia, H.; Albornoz, A. *J. Appl. Polym. Sci.* **1987**, *34*, 977.
- Wang, J. G.; Zhang, W. B.; Huang, B. T. *Makromol. Chem. Macromol. Symp.* **1992**, *63*, 245.
- Koivumaki, J.; Seppala, J. V. *Macromolecules* **1993**, *21*, 5535.
- Kim, J. A.; Jeong, Y. T.; Woo, S. I. *J. Polym. Sci. A Polym. Chem.* **1994**, *32*, 2979.
- Busico, V.; Cipullo, R.; Ronca, S. *Macromolecules* **2002**, *35*, 1537.
- Busico, V.; Cipullo, R.; Talarico, G.; Polzone, C.; Chadwick, J. C. *Macromolecules* **2003**, *36*, 2616.
- Busico, V.; Chadwick, J. C.; Cipullo, R.; Ronca, S.; Talarico, G. *Macromolecules* **2004**, *37*, 7437.
- Kissin, Y. V.; Rishina, L. A. *Polym. Sci. Ser. A.* **2008**, *50*, 1101.
- Zhang, L. T.; Fan, Z. Q.; Fu, Z. S. *Chinese J. Polym. Sci.* **2008**, *26*, 605.
- Fan, Z. Q.; Zhang, L. T.; Fu, Z. S. *J. Mol. Catal. A Chem.* **2011**, *351*, 93.

35. Zhang, L. T.; Fu, Z. S.; Fan, Z. Q. *Macromol. Res.* **2010**, *18*, 695.
36. Zhang, L. T.; Fan, Z. Q.; Fu, Z. S. *e-Polymer.* **2008**, *143*.
37. Kissin, Y. V. *Makromol. Chem. Macromol. Symp.* **1993**, *66*, 83.
38. Kissin, Y. V. *Macromol. Symp.* **1995**, *89*, 113.
39. Soares, J. B. P.; Hamielec, A. E. *Polymer.* **1995**, *36*, 2257.
40. Fan, Z. Q.; Feng, L. X.; Yang, S. L. *J. Polym. Sci. A Polym. Chem.* **1996**, *34*, 3329.
41. Kissin, Y. V.; MINK, R. I. *J. Polym. Sci. A Polym. Chem.* **2010**, *48*, 4219.
42. Kissin, Y. V. *J. Polym. Sci. A Polym. Chem.* **2003**, *41*, 1745.
43. Thompson, D. E.; McAuley, K. B.; McLellan, P. J. *Macromol. React. Eng.* **2007**, *1*, 264.
44. Song, B. G.; Choi, Y. H.; Ihm, S. K. *J. Polym. Sci. A Polym. Chem.* **2013**, *51*, 851.
45. Kakugo, M.; Miyatake, T.; Naito, Y.; Mizunuma, K. *Macromolecules.* **1988**, *21*, 314.
46. Xu, J. T.; Yang, Y. Q.; Feng, L. X.; Kong, X. M.; Yang, S. L. *J. Appl. Polym. Sci.* **1996**, *62*, 727.
47. Xu, J. T.; Feng, L. X.; Yang, S. L.; Yang, Y. Q.; Kong, X. M. *Macromolecules.* **1997**, *30*, 7655.
48. Xu, J. T.; Feng, L. X.; Yang, S. L.; Yang, Y. Q.; Kong, X. M. *Eur. Polym. J.* **1998**, *34*, 431.