

DEPENDENCE OF THE DISTRIBUTION OF ACTIVE CENTERS ON MONOMER IN SUPPORTED ZIEGLER-NATTA CATALYSTS*

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Abstract Distribution of active centers (ACD) of ethylene or 1-hexene homopolymerization and ethylene-1-hexene copolymerization with a $\text{MgCl}_2/\text{TiCl}_4$ type Z-N catalyst were studied by deconvolution of the polymer molecular weight distribution into multiple Flory components. Each Flory component is thought to be formed by a certain type of active center. ACD of ethylene-1-hexene copolymer with very low 1-hexene incorporation was compared with that of ethylene homopolymer to see the effect of introducing α -olefin on ethylene polymerization. On the other hand, ACD of ethylene-1-hexene copolymer with very low ethylene incorporation was compared with that of 1-hexene homopolymer. Adding small amount of 1-hexene in ethylene polymerization caused marked activation of all the Flory components of the polymer, in which the low molecular weight components are activated more than the high molecular weight components. In 1-hexene polymerization system, the activity can also be greatly enhanced by introducing small amount of ethylene, but the different Flory components (or active centers) are activated with similar extent, except a newly emerged active center producing polymer with the lowest molecular weight. The total number of active centers is markedly increased by adding small amount of ethylene in 1-hexene polymerization, but the average catalysis efficiency of the active centers decreased. The broad composition distribution of the ethylene-1-hexene copolymer can be well understood from the ACD of catalyst and its dependence on the monomer.

Keywords: Supported Ziegler-Natta catalyst; Active center distribution; Monomer.

INTRODUCTION

Heterogeneous Ziegler-Natta catalysts have the nature of multiple active centers^[1–5]. There is a distribution of active centers (ACD), which results in several peculiar features of the polymerization products, such as broad molecular weight distribution (MWD) and broad chemical composition distribution (CCD).

There are several influences of broad ACD on polymerization behaviors of heterogeneous Ziegler-Natta catalysts. Firstly the polymerization kinetics is more complicated. Co-existence of stable and unstable active centers may cause changes of polymer structure with reaction time. Secondly, molecular weight distribution is broad and poorly controllable. As a result, the mechanical properties and solvent resistance are lower and processing properties is fair but hard to regulate. Thirdly, the distribution of stereoregularity of poly(α -olefin) becomes poorly controlled. Presence of non-stereospecific centers makes further improvement of isotacticity very difficult. Finally, different types of active centers produce very broad copolymer composition distribution. The broad composition distribution strongly influences mechanical and processing properties, and increase solvent extractable. For example, linear low density polyethylene (LLDPE) synthesized by a single Ziegler-Natta (Z-N) catalyst in a single reactor always has its α -olefin comonomer concentrated in the low molecular weight part, but for high performance LLDPE an opposite CCD is needed.

To find out correct ways to regulate the active center distribution of ethylene- α -olefin copolymerization

* This work was supported by the Major State Basic Research Programs (No. 2005CB623804).

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Invited lecture presented at the Asian Polyolefin Workshop 2007, 2007, Hangzhou, China

Received March 17, 2008; Revised April 30, 2008; Accepted May 8, 2008

system, the following knowledge is definitely important: (1) How do the different active centers respond to addition of α -olefin comonomer into an ethylene polymerization system? (2) What types of active center show higher α -olefin incorporation rate, and why can they incorporate more α -olefin?

The important first step in solving these problems is to find the correlation between CCD and ACD^[1]. ACD analysis based on MWD deconvolution is a much available approach to the solution. There have been many literatures proving that the MWD of polymer produced by Z-N catalysts can be fitted by multiple Flory distribution curves^[1, 6, 7].

In this paper, systematical studies on ACD of ethylene-1-hexene copolymerization with a $\text{MgCl}_2/\text{TiCl}_4$ type Z-N catalyst were made to solve the above questions. At first, ACD of ethylene-1-hexene copolymerization with very low 1-hexene incorporation was compared with that of ethylene homopolymerization to see the effect of introducing α -olefin on ethylene polymerization. On the other hand, ACD of ethylene-1-hexene copolymerization with very low ethylene incorporation was compared with that of 1-hexene homopolymerization. In this way, we expect to get a better insight into the correlation between CCD and ACD as well as the nature of the active centers. MWD deconvolution has been used as the main method of ACD analysis.

EXPERIMENTAL

Preparation of Catalyst

A simple $\text{TiCl}_4/\text{MgCl}_2$ supported Z-N catalyst was prepared through reaction of $\text{MgCl}_2\cdot\text{EtOH}$ adduct with TiCl_4 . The preparation procedures and characterization of the catalysts are the same as described in a published paper^[5].

Polymerization

All polymerizations were carried out in a Schlenk flask which was evacuated and purged by N_2 for three times. *n*-Heptane as solvent, a designated volume of 1-hexene and $\text{Al}(i\text{-C}_4\text{H}_9)_3$ (TIBA, Albemarle Co.) were successively added into the Schlenk flask. Ethylene at 0.1 MPa (or 0.02 MPa) was continuously supplied to the flask. 20–30 mg of catalyst was added into the flask to catalyze the polymerization. At the end of polymerization, ethylene was stopped and the slurry was poured into 500 mL ethanol containing 2.5 mL hydrochloric acid to terminate the reaction and settling down the polymer. The polymer particles were filtered, washed with ethanol and dried in vacuum at 50°C.

Measurement of the Number of Active Centers

(Co)polymerization of 1-hexene or 1-hexene/ethylene was carried out in a 250 mL cylindrical reactor at 40°C. The reagents were added in the order of solvent, monomer, AlEt_3 , and the catalyst. After 5–10 min of polymerization, cinnamoyl chloride (in cinnamoyl chloride/Al (molar ratio) = 3–5) was injected into the reactor to quench the polymerization. After 10 min of quenching reaction, isopropyl alcohol/HCl mixture was added to decompose the catalyst, and the polymer was precipitated with excess of isopropyl alcohol. The polymer after purification was dried in vacuum at 60°C. The carbonyl (cinnamoyl) content in the quenched polymer was determined spectrophotometrically by a Varian Cary 100 Bio UV-Vis spectrometer. According to our previous work, each carbonyl group in the quenched polymer corresponds to an active center^[1, 8].

Copolymer Characterization

The polymer molecular weight and molecular weight distribution were measured by GPC in a PL 220 instrument (Polymer Laboratories Ltd.) at 150°C in 1,2,4-trichlorobenzene.

The ^{13}C -NMR (75 MHz) spectra of the copolymer were recorded at 130°C on a Varian mercury 300 plus NMR spectrometer^[5].

The copolymer samples were extracted by boiling *n*-heptane in Kumagawa extractor for 24 h to get two fractions (soluble and insoluble parts in boiling *n*-heptane). The soluble part was precipitated by ethanol. Both the soluble and insoluble parts were collected for GPC and NMR characterization.

RESULTS AND DISCUSSION

General Characteristics of the Copolymer

An ethylene-1-hexene copolymer was synthesized using the $\text{TiCl}_4/\text{MgCl}_2$ catalyst under typical conditions. The copolymer was fractionated into boiling *n*-heptane soluble and insoluble fractions, and the two fractions were characterized by ^{13}C -NMR and GPC. Table 1 lists the chain structure parameters of the copolymer and its fractions.

Table 1. Chain structure characteristics of an ethylene-1-hexene copolymer^a

Catalyst	Activity (kg PE/g Cat·h)	[H] ^c (mol%)	Boiling <i>n</i> -heptane insoluble fraction			
			Amount (wt%)	[H] (mol%)	$M_w \times 10^{-5}$	PDI ^d
$\text{TiCl}_4/\text{MgCl}_2^b$	0.62	6.65	71.9	1.78	5.49	6.6
Boiling <i>n</i> -heptane soluble fraction						
			Amount (wt%)	[H] (mol%)	$M_w \times 10^{-5}$	PDI ^d
			28.1	19.1	1.21	8.0

^a Copolymerization conditions: ethylene pressure = 0.1 MPa; $[\text{1-Hexene}]_0 = 0.2$ mol/L; $\text{Al}(i\text{-Bu})_3$ as cocatalyst, $x(\text{Al})/x(\text{Ti}) = 100$; $T = 50^\circ\text{C}$, time = 0.5 h; Solvent: *n*-heptane; ^b Ti content of the catalyst is 8.2 wt%; ^c 1-Hexene content of the copolymer determined by ^{13}C -NMR; ^d PDI = polydispersity index

It is seen in Table 1 that the 1-hexene content of the *n*-heptane soluble fraction (HS) is 10 times higher than that of the *n*-heptane insoluble fraction (HI), and the molecular weight of HI is higher than that of HS fraction. The chain structure of the copolymer showed a greatly heterogeneous character, which has been recognized long time ago. In general, 1-hexene is mainly incorporated in the low molecular weight fractions of the copolymer. Because of the great difference between the α -olefin incorporation rate of the two fractions, it is reasonable to assume the presence of two active center families in the catalyst.

ACD Analysis

To systematically study the influences of monomer on the ACD of supported Z-N catalyst, an ethylene- α -olefin copolymer with low 1-hexene incorporation was synthesized, with ethylene homopolymerization as the reference point. On the other end of the comonomer composition range, an ethylene- α -olefin copolymer with low ethylene incorporation was synthesized, with 1-hexene homopolymerization as the reference point. The molecular weight and MWD of the four polymer samples were measured by GPC, and the results, together with the polymerization activity data, were showed in Table 2. It is seen that addition of only 0.05 mol/L of 1-hexene in the ethylene polymerization system caused remarkable increase of polymerization activity from 3.12 kg PE/(g Ti·h) to 28.6 kg PE/(g Ti·h). Similar α -olefin activation effects (comonomer effect) have been found in many heterogeneous Ziegler-Natta catalysis systems^[9–12]. Kissin *et al.* ascribed this effect to reactivation of dormant $\text{Ti}-\text{CH}_2\text{CH}_3$ species through the insertion of an α -olefin^[3]. It can also be seen that the addition of 1-hexene led to a distinct decrease of molecular weight of copolymer. On the other side, there is also a strong activation effect when small amount of ethylene is introduced in the 1-hexene polymerization system. In this case a distinct decrease of molecular weight by ethylene addition is also observed. There seems to be another kind of comonomer effect when small amount of ethylene is added to an α -olefin polymerization system.

Table 2. (Co)polymerization behaviors under different monomer conditions

Monomer	Activity (kg PE/(g Ti·h))	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	PDI
Ethylene (0.02 MPa)	3.12	3.02	15.01	4.98
Ethylene (0.02 MPa) + 1-Hexene (0.05 mol/L)	28.6	0.66	4.72	7.19
1-Hexene (1 mol/L) + Ethylene (0.02 MPa)	23.6	1.56	7.22	4.64
1-Hexene (1 mol/L)	2.95	2.76	9.90	3.59

Copolymerization conditions: $\text{Al}(i\text{-Bu})_3$ as cocatalyst, $x(\text{Al})/x(\text{Ti}) = 150$; $T = 70^\circ\text{C}$, time = 5–10 min; Solvent: *n*-heptane

Figure 1 shows the MWD curves of the four polymer samples in Table 2 and the results of their MWD deconvolution with multiple Flory components. The two homopolymers (polyethylene and poly(1-hexene)) are all fitted by four Flory components (Figs. 1a and 1b), which are named as A, B, C and D. This means that there are four types of active centers in the homopolymerization systems. When small amount of a comonomer (ethylene or 1-hexene) were added in the system, an extra Flory component, peak E, appeared (Figs. 1c and 1d).

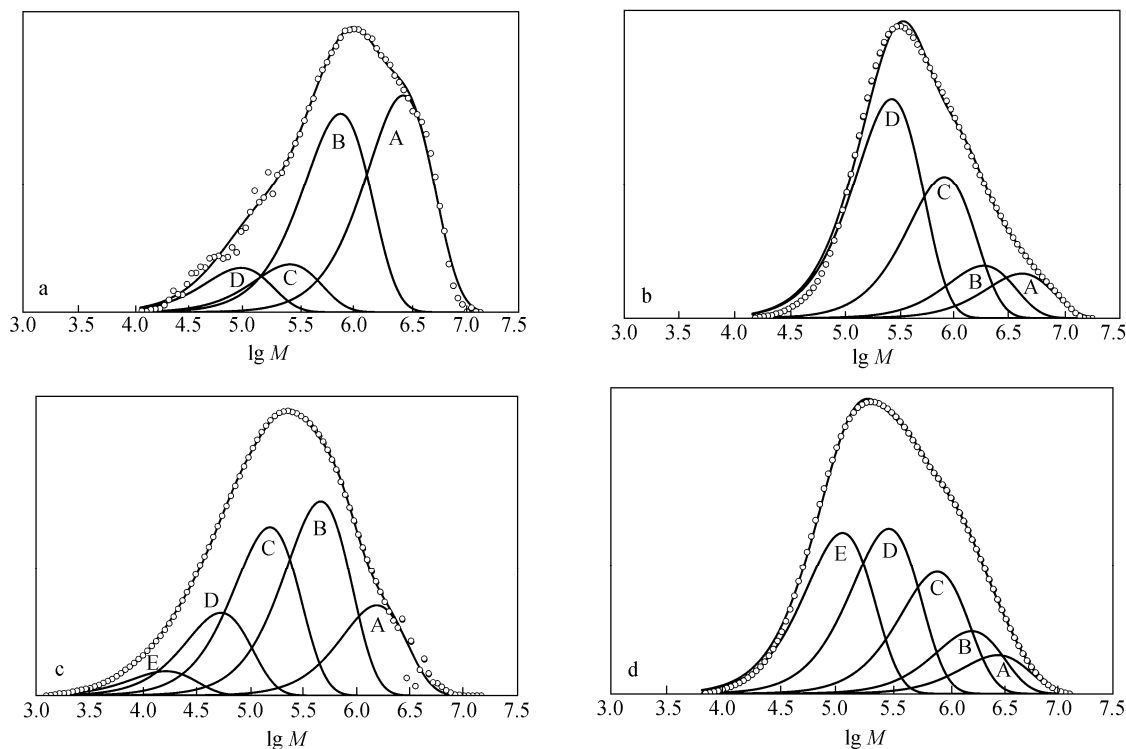


Fig. 1 MWD curve (circles) and its Flory components of (a) polyethylene (ethylene pressure = 0.02 MPa), (b) poly(1-hexene), ([1-hexene] = 1 mol/L), (c) ethylene-1-hexene copolymer (ethylene pressure = 0.02 MPa, [1-hexene] = 0.05 mol/L), (d) ethylene-1-hexene copolymer (ethylene pressure = 0.02 MPa, [1-hexene] = 1 mol/L). Polymerization conditions are the same as Table 2.

What is more meaningful is the relative weight of the Flory components in a certain sample, or the ACD. There are great differences in ACD between the ethylene and 1-hexene homopolymerization systems. In ethylene polymerization, the Flory components A and B representing the high molecular weight part are much larger than the components C and D at the low molecular weight side. In contrast, the poly(1-hexene) has C and D components much larger than the A and D components. Therefore, the four types of active centers may be divided into two families, one can efficiently catalyze ethylene polymerization (A and B) while the other can efficiently catalyze α -olefin polymerization (C and D). This great activity discrepancy between the two families of active centers and its sensitive change with monomer should be the main origin of the composition heterogeneity of the ethylene- α -olefin copolymers.

The subtle change of ACD by addition of a comonomer is also very interesting. After adding a small amount of 1-hexene in ethylene polymerization, the relative intensity of components C, D and E increased remarkably. This can be ascribed to the relatively higher activity of these active centers to α -olefin polymerization. On the other side, adding a small amount of ethylene in the 1-hexene polymerization system caused more complicated changes in ACD. The relative intensity of components A and B increased slightly, meanwhile a new component E emerged and became the largest one. The increase of A and B components (or A

and B type active centers) can be explained by their ability to catalyze ethylene faster than 1-hexene, but the emerging of active center E should be related to some kind of activation effects. However, it is quite clear that 1-hexene is mainly copolymerized in active centers C, D and E, while ethylene is mainly copolymerized in centers A and B. In such a case, the copolymer composition distribution shown in Table 1 can be reasonably explained, that is, the *n*-heptane soluble fraction is mainly composed of polymer from the C, D and E centers, and the *n*-heptane insoluble fraction is mainly composed of polymer from the A and B centers.

The activation effects (or the commoner effects) can also be understood better by analyzing the polymerization activities of the different Flory components and their changes with the monomer. Figure 2 compares the activities of the Flory components of the ethylene or 1-hexene homopolymer and the two copolymers. Adding small amount of 1-hexene in the ethylene polymerization system resulted in dramatic activation of all the active centers. The extent of activation varied with the type of active center and decreased in the order of: $E > D, C > B > A$. As proposed by Kissin *et al.*, the nature of the α -olefin activation effect is release of dormant $Ti-CH_2CH_3$ species^[3]. It seems that all the five types of active centers can rest in dormant state in ethylene polymerization, but their extent of dormancy differ from each other. The centers E, D and C may be more dormant than the centers A and B.

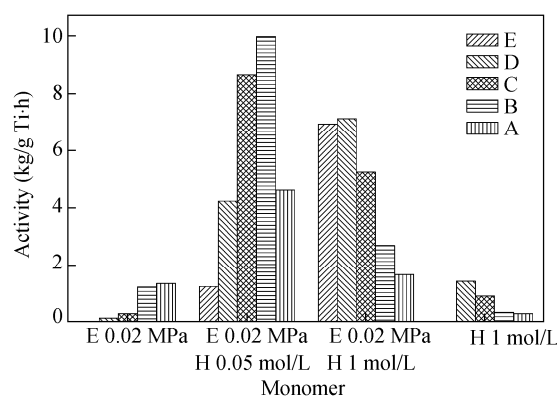


Fig. 2 Activity of the Flory components in the four polymers

As shown in Fig. 2, small amount of ethylene can also greatly activate 1-hexene polymerization, but in this case the centers A, B, C and D are activated with roughly the same extent. The new active center E is totally released by the by ethylene, but its intensity became the second largest among the five active centers. Such activation of α -olefin polymerization by ethylene might be explained by reactivation of dormant active centers $Ti-CH(R)-CH_2-P$ after insertion of an ethylene unit. These kind of dormant centers are formed when a secondary insertion of α -olefin happens^[13–15].

By comparing the ACD of the above four polymers, it is clear that both ethylene and 1-hexene plays the role of activating the chain propagation of the other monomer in their copolymerization system, though their activation mechanism may be quite different.

Effects of Monomer on the Number of Active Centers

To further understand the mechanism of ACD dependence on the monomer, the number of active centers of a 1-hexene homopolymerization and a 1-hexene-ethylene copolymerization system were determined by the acyl chloride quenching method, and the results are listed in Table 3.

As shown in Table 3, adding small amount of ethylene in 1-hexene polymerization system caused marked increase in the number of active centers. This means that some more active centers were activated in the copolymerization. Though the polymerization activity increased after adding ethylene, the catalysis efficiency of the active centers decreased. Therefore, the newly released active center should be less active than the centers working in 1-hexene homopolymerization system. On the other hand, the molecular weight and isotacticity of

the poly(1-hexene) segments also decreased after ethylene addition. Considering the change in ACD caused by small amount of ethylene in 1-hexene polymerization system, it is reasonable to assume that the newly emerged center E has lower inherent activity and stereospecificity than the other types of active centers. To know more about the differences in number, activity and other properties between the five types of active centers, a direct ACD analysis based on determination of the number of active center in different polymer fractions is underway, and the results will be reported soon.

Table 3. Effects of monomer on the number of active centers

Run	P_E^a (MPa)	Activity (kg PH/(g Ti·h))	C^*/Ti^b (mol%)	Efficiency (kg PH/mol $C^*·h$)	$M_w \times 10^{-4}$	PDI	$[E]^c$ (%)	[mmmm] ^d (%)
4	0	4.5	0.24	90000	3.50	4.92	0	64.1
5	0.01	7.1	0.57	60000	3.15	4.60	3.1	59.2

Conditions: $TiCl_4/MgCl_2-AlEt_3$; $T_p = 40^\circ C$; 6 min; $[1-Hexene]_0 = 1$ mol/L; $x(Al)/x(Ti) = 50$;

^a Ethylene pressure; ^b Number of active centers expressed as the percentage of active center in titanium;

^c Ethylene content of the copolymer determined by ^{13}C -NMR; ^d Isotactic pentad content of the poly(1-hexene) segments determined by ^{13}C -NMR

CONCLUSIONS

In conclusion, the active center distribution of $TiCl_4/MgCl_2$ type Z-N catalysts is strongly related to the kind of monomer. Adding small amount of 1-hexene in ethylene polymerization cause marked activation of all the Flory components of the polymer, in which the low molecular weight components are activated more than the high molecular weight components. In 1-hexene polymerization system, the activity can also be greatly enhanced by introducing small amount of ethylene, but the different Flory components (or active centers) are activated with similar extent, except a newly emerged active center producing polymer with the lowest molecular weight. The total number of active centers is markedly increased by adding small amount of ethylene in 1-hexene polymerization, but the average catalysis efficiency of the active centers decreased.

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