

Cite this: *Polym. Chem.*, 2012, **3**, 2377

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PAPER

A new high-performance Ziegler–Natta catalyst with vanadium active component supported on highly-dispersed MgCl_2 for producing polyethylene with broad/bimodal molecular weight distribution

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Received 20th March 2012, Accepted 9th June 2012

DOI: 10.1039/c2py20163a

In this paper, we synthesized a highly-dispersed MgCl_2 support using the Grignard reagent method, and loaded it with TiCl_4 and VCl_4 to prepare polyethylene catalysts with titanium and vanadium active centers. The two catalysts demonstrated narrow particle distribution. The polymerization data demonstrated that the two catalysts both had good activity. And GPC and ^{13}C NMR data indicated that polymer produced with vanadium active centers has some good characteristics, a broader molecular weight distribution and higher degree of methyl branching compared with polymer produced by catalysts with titanium active centers. Also, we found that the molecular weight distribution can be controlled by changing the hydrogen pressure in polymerization; because of the dual active sites have different responses to hydrogen pressure. Also, through ^{13}C NMR data, we found that most of the methyl branching occurred in the high molecular weight part. The existence of methyl branching in the high molecular weight part and broader molecular weight distribution of polyethylene can solve the contradiction of mechanical properties and processing properties.

1. Introduction

With the increasing of polyethylene (PE) application, PE with high strength and excellent processing performance surges in demand. Polyethylene's molecular weight distribution (MWD) and short chain branching at high molecular weight part have a significant influence on the product's melt flow index and mechanical properties. It can solve the contradiction between the workability and strength of the polyethylene, resins with these features have good mechanical properties and toughness, are easy to process and so on.

Although the Ziegler–Natta catalyst with a titanium active center is well known in polyolefins, polyethylene products using this catalyst have a narrow molecular weight distribution ($\text{MWD} = 4\text{--}8$)¹ and generally poorer processability. It is very important to control MWD and short chain branching (SCB) distribution for high density polyethylene (HDPE) for pipe applications.^{2,3} A general method to produce polyethylene with

broad/bimodal MWD and SCB over titanium–magnesium catalyst is tandem reactors with different polymerization conditions.

The nature of the active component may exert a considerable effect on the molecule mass characteristics of PE and ethylene- α -olefin copolymers. In particular, supported vanadium–magnesium catalysts (VC) containing vanadium chloride as the active component supported on MgCl_2 differ considerably from titanium–magnesium catalysts (TC) regarding the regulation of molecular structure of PE and copolymers of ethylene with α -olefin.^{1,4–13} Unlike TC, VC produced PE with broad MMD.^{5–13} In addition, VC had a very high hydrogen response and provided an effective control of PE molecule mass in ethylene polymerization with hydrogen.^{12,13}

In the literature there are limited data on the study of polymerization conditions on MWD and nature of chain branching and chain branching distribution for PE produced with VC. We have obtained new data on the MMD and molecular structure of PE produced over new modifications of highly active vanadium–magnesium catalysts (VC) (average particle size is 5 μm , narrow particle size distribution) in ethylene polymerization with different hydrogen concentrations. ^{13}C NMR method has been used for the analysis of branching in PE. With using GPC data on the molecular mass (M_n) of PE, we have estimated the amount of branches in polymer chains. These data have been compared with respective data for PE prepared over TC.

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2. Experimental

2.1. Materials

All experiments were performed under nitrogen atmosphere. Ethylene (>99.95% purity; <3 ppm H₂O, <5 ppm O₂), nitrogen (>99.99% purity; <2 ppm H₂O, <0.5 ppm O₂), hydrogen (>99.99% purity; <3 ppm H₂O, <2 ppm O₂), butene-1 (>99% purity; <2.5 ppm H₂O), hexane (<3 ppm H₂O) were purified in the factory and were used as received. Magnesium powder particle size is 70–100 µm. Butyl chloride (99%, Aldrich), dibutyl ether (99%, Aldrich) chlorobenzene (99%, Aldrich) and carbon tetrachloride (99%, Aldrich) were treated by 4A molecular sieves with metal M_n to remove water and oxygen. Vanadium tetrachloride (Aldrich), diethylaluminum chloride (1.1 M solution in toluene, ACROS ORGANICS) and triisobutylaluminum (TiBA, 1.1 M solution in toluene, ACROS ORGANICS) were used as received.

2.2. Catalyst preparation

Supported catalysts were synthesized *via* the procedure described in the literature.¹⁴ Highly active supported catalysts VC and TC were synthesized by supporting VCl₄ or TiCl₄ on highly dispersed MgCl₂. This support had been prepared by chlorination of a chlorobenzene solution of an organomagnesium compound (Mg₃Ph₄Cl₂) by PhCCl₃ in the presence of dibutyl ether. Washed support was treated with AlEt₂Cl and CCl₄ (Al/Mg molar ratio = 1.2; CCl₄/Mg molar ratio = 0.1; 45 °C). Magnesium chloride support contains 1.5 wt % of aluminum and exhibits a narrow particle size distribution; average particle size of this support was about 5 µm. The VC catalyst was prepared by treating the support with vanadium tetrachloride at room temperature, reacting for 1 h (V/Mg molar ratio = 0.075; 60 °C), followed by washing with hexane. The catalyst contains 3 wt% of vanadium. The catalyst TC was prepared by treating the support with titanium tetrachloride at room temperature, reacting for 2 h (60 °C), followed by washing with hexane. The catalyst contains 3 wt% of titanium.

2.3. Polymerization

Ethylene slurry polymerization was carried out in a 2 L stainless steel reactor. The reactor was equipped with an external heating jacket heater and an internal cooling coil that kept the polymerization temperature. It was also equipped with a magnetic coupled stirrer with variable stirring speed. A pressure sensor was used to keep the polymerization pressure by a controlling ethylene valve;

also, a temperature sensor was used to keep the polymerization temperature by controlling heat and cool water valve.

The polymerization conditions were as follows: hexane was used as solvent (1 L); polymerization temperature was 80 °C; polymerization pressure was 1 MPa; hydrogen was charged into the reactor at the beginning of the polymerization; TiBA (triisobutylaluminum) was used as a co-catalyst (4.8 mmol L⁻¹). The reaction time was 2 hours.

2.4. Measurements

The vanadium concentration and aluminum concentration in the catalyst were determined by AES-ICP (Optima 5300DV spectrometer, PE Corporation, USA).

As specified in the ASTM test, melt index (MI) of polyethylene was measured with the weights of 5 Kg (MI_{5Kg}) and 21.6 Kg (MI_{21.6Kg}) at 190 °C, the results were expressed in g per 10 min. The melt flow ratio (MFR) was the ratio of MI_{21.6 kg}/MI_{5 kg}.

Molecular weight (M_w, M_n, M_z) and molecular weight distribution (MWD) were measured using a WATERS 150 C gel permeation chromatography (GPC) equipment (Waters Corporation, Milford, MA, USA) in conjunction with a Viscotek Model 100 differential viscometer (Viscotek Benelux BV, TW Oss, the Netherlands) at 140 °C and calibrated with polystyrene standards. The 1,2,4-trichlorobenzene was used as a solvent; four mixed-bed TSK-gel columns (GMHXL-HT, Tosoh Corp, Tokyo, Japan) were used at a flow rate of 1 cm³ min⁻¹.

¹³C NMR measurement was carried out with a Mercury-300 (Vrian Corporation, USA) at 110 °C. Samples were dissolved in *o*-dichlorobenzene, concentration ranging from 0.05 to 0.12 g mL⁻¹.

3. Results and discussion

Table 1 shows the properties of PE produced with VC and TC catalysts. It can be seen that the two catalysts exhibit similar activities. But the polyethylene product made with VC (VC-PE) has some features. VC has a good hydrogen regulating sensitivity, increasing the hydrogen pressure by a small amount can lead to MI ratio increasing sharply; also, VC-PE also has a broader MWD and high degree of branching.

3.1. Molecular weight distribution of polyethylene

Fig. 1 presents the GPC data for the polyethylene produced with VC and TC catalysts. Significant differences between the GPC data for these two polymers were observed. VC produced PE

Table 1 Characteristics of PE samples produced over VC and TC catalysts at the ethylene polymerization with different hydrogen concentration^a

Exp. no.	Cat.	PH ₂ (MPa)	Activity (kgPE/gCat.)	MI _{21.6 kg} (g/10 min)	MFR	MWD	C=C/1000C	CH ₃ /1000C
1	VC	0.03	14.2	0.6	26.9	13.0	<0.01	<0.1
2		0.05	9.9	8.8	21.5	16.3	0.02	3.5
3		0.08	9.1	31.8	18.6	17.3	0.02	4.7
4		0.10	9.0	43.5	16.0	19.3	0.02	5.8
5	TC	0.05	15.7	0.6	8.5	4.6	0.06	<0.1
6		0.15	10.8	7.3	11.6	5.8	0.05	0.3
7		0.25	9.3	25.0	10.4	5.1	0.07	0.9
8		0.30	6.6	47.4	10.6	5.1	0.06	1.0

^a Experimental conditions: TiBA as co-catalyst, its concentration is 4.8 mmol L⁻¹, $\sum P$ = 1.0 MPa, polymerization at 80 °C, 2 h. GPC analysis used universal calibration.

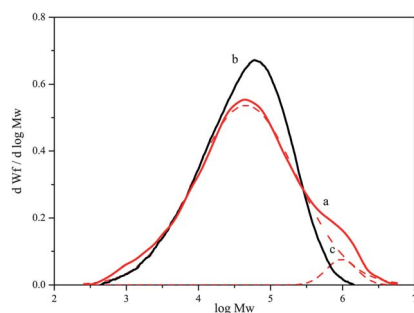


Fig. 1 MWD of polyethylene produced with VC and TC catalyst. (a) Catalyst: VC, $\text{PH}_2 = 0.10$ MPa; (b) catalyst: TC, $\text{PH}_2 = 0.30$ MPa; (c) Gaussian fitting line for curve a. Experimental conditions: TiBA as co-catalyst, its concentration is 4.8 mmol L^{-1} , $\sum P = 1.0$ MPa, polymerization at 80°C , 2 h.

with broader bimodal MMD. M_w/M_n for VC-PE was equal to 19.3, in contrast to 5.1 for PE synthesized with TC (TC-PE). We can see clearly that VC-PE had a shoulder within the high molecular weight region (Fig. 1, curve a) compared with TC-PE (Fig. 1, curve b). These data suggested that the VC catalyst had two different active sites. One active site (CP1) can produce PE with lower molecular weight; the other active site (CP2) can produce PE with higher molecular weight. To prove the presence of different active sites, we did some research.

Through our research, polymerization temperature, pressure, co-catalyst concentration and co-polymerization monomer concentration have little impact on MWD. But hydrogen pressure has a significantly effect on MWD of VC-PE.

Tables 1 and 2 illustrate the effect of the hydrogen pressure on the molecular weight and MWD of PE produced with VC. It can be seen that increase hydrogen pressure caused decrease molecular weight and broadening MWD of PE. Fig. 2 and Table 2 shows that as hydrogen pressure increased, the peak in low molecular weight (P1) shifted to lower weight region, while the peak in high molecular weight (P2) remained in the same position, about $M_w = 550 \times 10^3$. These data show there were different active sites with different responses to hydrogen pressure in this catalyst. With increasing hydrogen pressure, P2 remained in the same position and its area decreased, this data indicated there was one active site that wasn't involved in the reaction of chain transfer

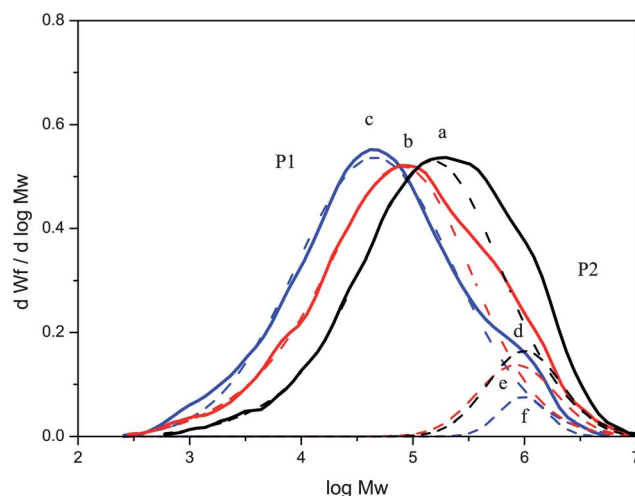


Fig. 2 MWD of polyethylene produced with VC catalyst under different hydrogen pressures. (a) $\text{PH}_2 = 0.03$ MPa; (b) $\text{PH}_2 = 0.05$ MPa; (c) $\text{PH}_2 = 0.08$ MPa; (d) Gaussian fitting line for curve a; (e) Gaussian fitting line for curve b; (f) Gaussian fitting line for curve c. Experimental conditions: TiBA as co-catalyst, its concentration is 4.8 mmol L^{-1} , $\sum P = 1.0$ MPa, polymerization at 80°C , 2 h.

in present of hydrogen, instead of decreased activity. P1 shifted to lower molecular weight, these data indicated this active center occurred chain transfer reaction with hydrogen.

General, multi-active sites that cause MWD broadening are usually attributed to different active sites at which different chain propagation reactions take place. However, the catalyst VC can produce broad MWD because of the chain transfer reaction with hydrogen. VC has two types of active sites, one active site (CP1) is very easy to involve in the chain transfer reaction and can produce PE of lower molecular weight with hydrogen. The other type of active sites (CP2) is not reactive in the chain transfer reaction and can produce PE of higher molecular weight with hydrogen. PE with high molecular weight has a lower fraction in the presence of hydrogen. In other words, CP2 decreased in activity quicker under hydrogen than CP1.

Kissin¹⁵ explained that catalysts with titanium active centers lose their activity during ethylene polymerization in the presence of hydrogen. Ethylene inserted along the Ti-H bonds to form the

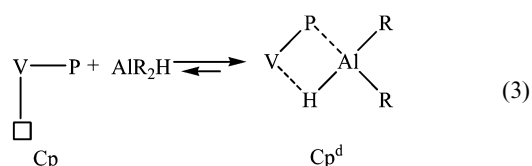
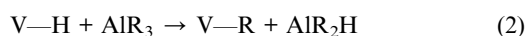
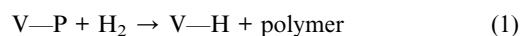
Table 2 Gaussian fitting data of Fig. 2^a

No.	PH_2 MPa	Peak	Area percent	Center value ($\log M_w$)	$M_n \times 10^3$	$M_w \times 10^3$	$M_z \times 10^3$	MWD
A	0.03	Initial	—	—	37	480	1800	13.0
		P1	86.2%	5.196	32	360	1850	11.5
		P2	13.8%	6.002	745	1300	2300	1.8
		Sum	100%	—	36	500	2000	13.8
B	0.05	Initial	—	—	19	310	1400	16.3
		P1	88%	4.939	15	195	1150	13.0
		P2	12%	5.927	610	1150	2100	1.9
		Sum	100%	—	17	310	1600	18.2
C	0.08	Initial	—	—	11	190	1050	17.3
		P1	95.9%	4.657	13	160	1100	12.3
		P2	4.1%	5.987	860	1100	1400	1.3
		Sum	100%	—	13	200	1150	15.4

^a Experiment conditions correspond to those in Fig. 2.

species $\text{Cl}_x\text{Ti}-\text{CH}_2\text{CH}_3$. During the polymerization dormant site $\text{Cl}_x\text{Ti}-\text{CH}_2\text{CH}_3$ was forming for ethylene insertion along the $\text{Ti}-\text{H}$ bonds. A lot of ethane will product for $\text{Cl}_x\text{Ti}-\text{CH}_2\text{CH}_3$ reacting with hydrogen. Ethylene polymerization at $\text{H}_2/\text{C}_2\text{H}_4 = 0.2$, about 20 vol% ethane was detected. Karol¹⁵ gave the proof for $\text{V}-\text{H}$ bonds also forming during the polymerization with hydrogen using the catalyst $\text{VCl}_3/\text{THF}/\text{SiO}_2/\text{AlEt}_2\text{Cl}$. In order to find the reasons for the VC catalyst's loss of activity in the presence of hydrogen, we have analyzed the composition of the reaction medium, at $\text{H}_2/\text{C}_2\text{H}_4 = 0.03-0.1$, ethane concentration never exceed 1 vol%. This experimental data shows that the ethylene hydrogenation reaction is not the reason for the deactivation of VC.

Mikenas *et al.*^{8,12} have studied hydrogen pressure effect to supported vanadium catalyst. And they had given the active center poisoning theory shown as eqn (1)–(3).



Chemical reaction in eqn (1) is the process of chain transfer for obtaining V–H bonds. In the reaction in eqn (2) surface vanadium hydrides reacted with co-catalyst (aluminum trialkyl) producing the monomer alkylaluminumhydride. This compound may react with active sites (Cp) to generate another compound (Cp^d). Cp^d is difficult to break down, it can block active site, and form inactive dormant sites.

This theory can explain our observations very well. The two active sites have different responses to reaction in eqn (3). Cp2 is

Table 3 Data on the composition of PE fractions

Polymer and catalyst ^a	Fraction	Fraction proportion, wt. %	Content CH ₃ /1000C
EXP. 1 VC	Total polymer	100	<0.1
	Heptane soluble ^b	3.1	7.3
	Heptane insoluble ^c	96.9	<0.1
EXP. 3 VC	Total polymer	100	5.1
	Heptane soluble ^b	26.5	9.9
	Heptane insoluble ^c	73.5	4.9
EXP. 6 TC	Total polymer	100	1.8
	Heptane soluble ^b	17.9	9.9
	Heptane insoluble ^c	82.1	<0.1

^a Numbers of experiments correspond to those in Table 1. ^b Fraction soluble in boiling heptane. ^c Fraction insoluble in boiling heptane.

more reactive to this step, and the forming of Cp^d leads to hydrogen's low effect on chain transfer reaction, so the fraction of high molecule decreased sharply, and molecular weight didn't decrease. But $\text{Cp}1$ involved in chain transfer reaction, molecular weight decreased. In summary, these two active sites' different response to the hydrogen caused broader molecular weight distribution.

3.2. Molecular structure of polyethylene

From Table 1 row 9, we can see that VC-PE has a high degree of branching compared with TC-PE. ^{13}C NMR given the data of branching type, VC-PE has a large number of methyl-branched-chain, and the concentration of methyl groups increases as the PE molecular weight decreases. In order to get more details of branches in VC-PE, we did the following experiments. Three VC-PE and TC-PE samples (Table 1, exp. no. 1, 3 and 6) were divided into two fractions by extraction with boiling heptane, and each fraction's methyl content was measured by ^{13}C NMR (Table 3).

The data in Table 3 (exp. 3 and 6) show that VC-PE content far exceeded more of methyl in heptane insoluble fraction compared with TC-PE, in other word, VC-PE polymerization in the presence of high hydrogen pressure has a higher degree of methyl branching than TC-PE in the high molecular weight fraction. But in the heptane soluble fraction, TC-PE has more methyl content. To determine the degree of polymer, we analyzed the heptane soluble polymer fractions ^{13}C NMR data. Fig. 3 and Fig. 4 show the ^{13}C NMR spectrum of TC-PE and VC-PE soluble fraction. The signal assignment presented in Table 4 and eqn (4) was done according to ref. 16.

The ^{13}C NMR spectrum of VC-PE soluble fraction exhibits extra signals at 19.96 ppm, 27.42 ppm, 30.36 ppm, 33.22 ppm and

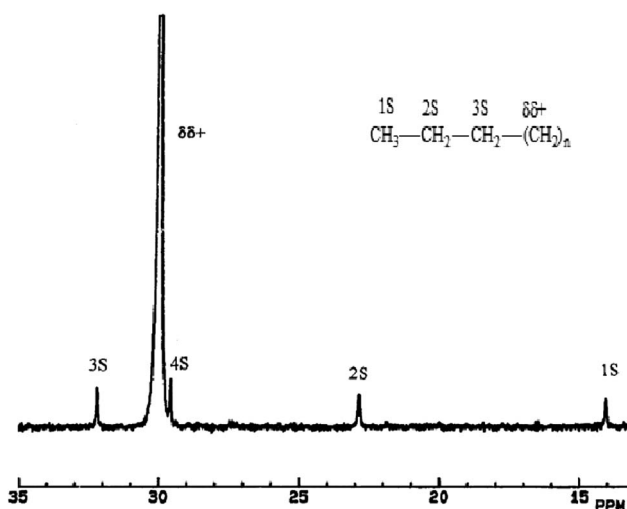
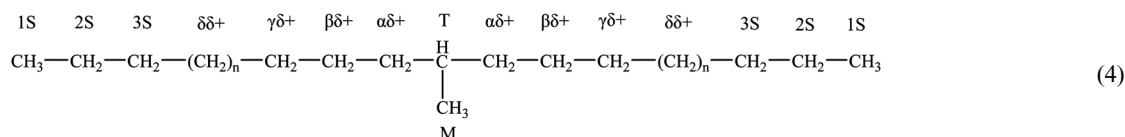


Fig. 3 ^{13}C NMR spectrum of the heptane-soluble fraction of TC-PE. (For signal assignments and integral intensities see Table 3, exp. 6).



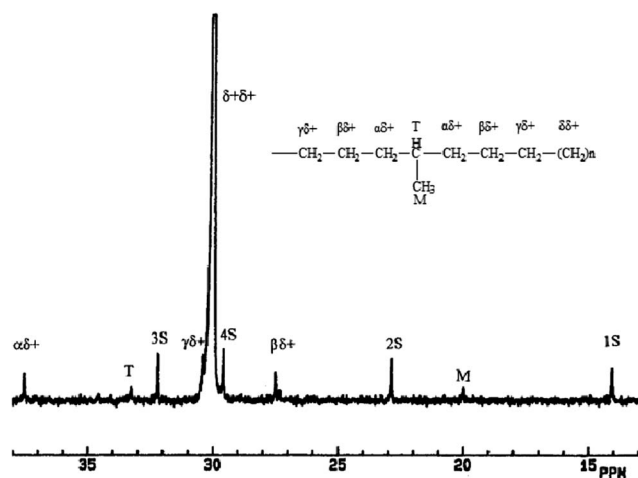


Fig. 4 ^{13}C NMR spectrum of the heptane-soluble fraction of VC-PE. (For signal assignments and integral intensities see Table 3, exp. 3).

37.51 ppm, compared with that for TC-PE. It can be ascribed to the existence of methyl branched fragments. Exp. 1 has a similar ^{13}C NMR spectrum to exp. 3, except for weaker signals at 19.96 ppm, 27.42 ppm, 30.36 ppm, 33.22 ppm and 37.51 ppm.

Table 4 ^{13}C NMR data for heptane-soluble fractions

Carbon	Chemical shift δ in ppm	Intensity in % ^a (exp. 1, VMC)	Intensity in % ^a (exp. 3, VMC)	Intensity in % ^a (exp. 6, TMC)
1S	14.05	0.71	0.67	0.98
2S	22.86	0.70	0.67	0.98
3S	32.18	0.71	0.66	0.99
4S	29.59	0.71	0.67	0.99
$\alpha\delta+$	37.51	0.05	0.66	0
T	33.22	0.02	0.34	0
$\gamma\delta+$	30.36	0.04	0.68	0
$\delta\delta+$	29.98	96.95	94.55	96.05
$\beta\delta+$	27.42	0.05	0.66	0
$\text{CH}_3(\text{M})$	19.96	0.02	0.33	0

^a Numbers of experiments correspond to those in Table 3.

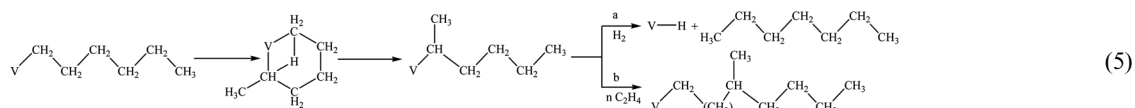
Table 5 Molecular structure of polyethylene calculated from ^{13}C NMR and GPC data

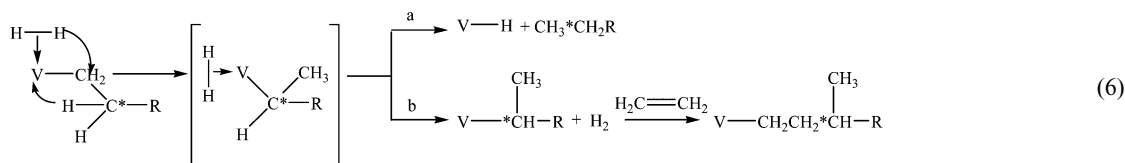
	Exp. 1 ^a VC		Exp. 3 ^a VC		Exp. 6 ^a TC	
	Polymer	Heptane soluble ^b	Polymer	Heptane soluble ^b	Polymer	Heptane soluble ^b
$\text{CH}_3/1000\text{C}$	<0.1	7.3	5.1	9.9	1.8	9.9
$\text{CH}_3(1\text{S})/1000\text{C}$	—	7.1	—	6.7	—	9.8
$\text{CH}_3(\text{M})/1000\text{C}$	—	0.2	—	3.3	—	0
$M_n \times 10^{-3}$ ^c	37	3.9	11	4.2	16	2.9
Branching CH_3 per polymer chain	—	0.1	2.0	1.0	0.1	0

^a Numbers of experiments correspond to those in Table 1. ^b Fraction soluble in boiling heptane. ^c The polymer's M_n was measured by GPC, the heptane soluble fraction's M_n was calculated from ^{13}C NMR data from the ratio of the end group intensities in the total intensity.

We can calculate the number average molecular weight of the fraction soluble in boiling heptane and estimate the content of methyl branches using the ^{13}C NMR data. For example, exp. 3 in Table 5, for polymer, $\text{CH}_3/1000\text{C} = 5.1$, according to GPC data, $M_n = 11\,000$, assuming that each polymer chain didn't have double bonds, contains 2 terminal CH_3 groups, every chain has 785.7 CH_2 groups on average, $1000/785.7 = 1.3$, so, $5.1/1.3 = 4.0$, besides two terminal CH_3 groups, each chain contains on average 2.0 extra methyl branches; for the heptane soluble fraction, $\text{CH}_3(1\text{S})/1000\text{C} = 6.7$, every chain has 2 terminal CH_3 groups, $6.7/2 = 3.4$, every chain has $1000/3.4 = 298.5$ carbons on average, $M_n = 4181$, $\text{CH}_3(\text{M})/1000\text{C} = 3.3$, so, each chain contains on average $3.3/3.4 = 1.0$ extra methyl branches.

From Table 5, we can see that VC-PE has higher degree of methyl branching in high molecular weight, and VC-PE has a better branching characteristic than TC-PE as well. Using gas chromatography, Kissin¹⁷ determined the composition of oligomers forming in ethylene polymerization with $\text{SiO}_2/\text{AlEt}_3/\text{VOCl}_3$ catalysts at 90 °C in the presence of hydrogen. The gas chromatography spectrum found methyl and ethyl branching in ethylene oligomers, and they were attributed to a widely recognized chain isomerization mechanism showed as eqn (5).





The data in Table 5 present that the degree of methyl branching grow as hydrogen pressure increases, so, VC-PE's high branching characteristic must have some relationship with hydrogen. Echevskaya¹⁸ has given another mechanism for VC-PE's high degree of branching, shown in eqn (6).

This mechanism can explain our data well, isomerization occurs when hydrogen reacts with active center, then the isomer may react through path a, it is chain transfer reaction, generate vanadium hydrogen bond and long-chain polymer; or react through path b, the isomer reacts with ethylene, the carbon chain grows and generates a chain with methyl branching.

4. Conclusions

The catalysts with vanadium and titanium active centers both behaved well in polymerization with hydrogen. So, the yield of PE produced over VC was 9–14 kg PE g⁻¹ cat. in 2 h (80 °C). The polymer produced by VC catalyst presents some good characteristics. From GPC data, we can see that because catalyst VC has dual active sites, the MWD of PE produced by VC is 15.7–19.3, compared with TC-PE's 4.6–5.1, broader molecular weight solved the contradiction of mechanical properties and processing performance. And ¹³C NMR dates indicated that VC-PE has a high degree of methyl branching, it's CH₃/1000C can achieve 4.7, through we didn't introduce comonomer during the polymerization. The existence of methyl branching improved the polymer processability effectively.

Acknowledgements

This work was supported by a research grant from China's Ministry of Science and Technology International Cooperation Project (Grant no. 2008DFR40400).

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