

ETHYLENE POLYMERIZATION AND ETHYLENE/HEXENE COPOLYMERIZATION WITH VANADIUM CATALYSTS BEARING THIOPHENOL- PHOSPHINE LIGANDS*

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Abstract Vanadium(III) complexes bearing thiophenol-phosphine ligands (**2a–2b**) (2-R-6-PPh₂-C₆H₂S) VCl₂(THF)₂ (**2a**: R = H; **2b**: R = Me₃Si) were prepared from VCl₃(THF)₃ by treating with 1.0 equiv of the ligand in tetrahydrofuran in the presence of excess triethylamine. The two complexes were characterized by FTIR and mass spectra as well as elemental analyses. On activation with Et₂AlCl, these complexes exhibited high catalytic activities (up to 22.1 kg PE/(mmol·h·bar)) even at high temperature (70 °C), and produced high molecular weight polymers with unimodal molecular weight distributions, indicating the polymerization took place in a single-site nature. This result may be attributed to benefits of introduction of second-row donor atoms for adjusting charge density of the vanadium centers. In addition, these complexes also exhibited high catalytic activities for ethylene/1-hexene copolymerization. Catalytic activity, comonomer incorporation and polymer molecular weight can be controlled in a wide range by the variation of catalyst structure and the reaction parameters such as Al/V molar ratio, comonomer feed concentration and polymerization reaction temperature.

Keywords: Ziegler-Natta polymerization; Vanadium catalyst; Polyethylene; Copolymerization.

INTRODUCTION

A significant number of advances in olefin polymerization catalysis have been reported in the past decade, and the development of new generation “non-metallocene” catalysts has attracted great interest recently^[1–5]. Among the transition metals, vanadium catalysts exhibited promising characteristics, especially for the syntheses of high molecular weight polyethylene, syndiotactic polypropylene, poly(ethylene-*co*-propylene) and poly(ethylene-*co*-propylene-*co*-diene) elastomers^[6–15]. However, catalyst deactivation at high reaction temperatures is an issue in polymerization with vanadium(III) complexes due to reduction of catalytically active vanadium species to low-valent, less active or inactive species. Therefore, the design and synthesis of new vanadium(III) catalysts with high thermal stability for olefin polymerization have attracted considerable attention^[16–22]. For example, Redshaw and his coworkers reported that vanadium complexes with calixarene ligands exhibited excellent performance in olefin polymerization catalysis^[23–25]. Nomura demonstrated that high catalytic activity and efficient α -olefin or cycloolefin incorporation could be obtained if the (arylimino)(aryloxo)vanadium complexes were used as catalyst precursors^[26–31]. Our group have synthesized and characterized a series of vanadium complexes bearing tetradentate trihydroxy amine ligands, which exhibit high catalytic activities for the

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copolymerization of ethylene with some polar norbornene derivatives^[32].

Introducing some softer second-row donors in the ligand is an effective method to offer beneficial stabilization of the highly reactive metal center^[33–35]. Our previous research indicated that bidentate [O,P] vanadium complexes through structural evolution displayed high activities and high 1-hexene incorporation for ethylene (co)polymerization^[36]. In addition, they could maintain a single-site catalytic behavior even at high temperatures during a long reaction time. Based on these facts, We tried to introduce another soft second-row donor, such as S atom into the ligands, expecting more thermally stable vanadium(III) complexes. So we have designed and synthesized a new kind of vanadium catalysts based on [S,P] ligands to study further how the soft donor may affect the non-metallocene vanadium catalysts on their olefin polymerization behavior. In this work, we try to find out the catalytic characteristics of [S,P] vanadium complexes by comparing with the [O,P] and [O,P=O] ones under the same condition. Next, this paper is focused on the performance of vanadium complexes in catalyzing ethylene/ α -olefin copolymerization. We also propose the chain transfer mechanisms by investigating the microstructure of ethylene/1-hexene copolymers.

EXPERIMENTAL

General

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry argon atmosphere using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun solvent purification system. The NMR data of the ligands were obtained on a Bruker 400 MHz spectrometer at ambient temperature with CDCl₃ as a solvent. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific).

Ethyl trichloroacetate (ETA) was purchased from Aldrich, dried over calcium hydride at room temperature, and then distilled. The *n*-butyllithium solution in hexane and VCl₃(THF)₃ was purchased from Aldrich. Et₂AlCl was purchased from Albemarle Corporation. Commercial ethylene was directly used for polymerization without further purification. The other reagents and solvents were commercially available. [S,P] ligands containing different substituent on R₁ and R₂ positions were prepared according to literature procedures^[37, 38].

Synthesis and Characterization of Vanadium Complexes

Complex 2a

To a stirred solution of VCl₃(THF)₃ (0.37 g, 1.0 mmol) in dried THF (20 mL) was added slowly a solution of **1a** (0.29 g, 1.0 mmol) in THF (20 mL). The red reaction mixture was stirred for 10 min, and Et₃N 10 mmol was added. After stirring for 4 h at room temperature the solution was concentrated to about 10 mL, and then filtered to remove NH₄Cl. Crystallization by diffusion of *n*-hexane (20 mL) into the clear solution yielded red-black crystals of **2a** (0.35 g, 63%). IR (KBr pellets): ν 3390, 3057, 2974, 2901, 1600, 1579, 1558, 1483, 1448, 1463, 1401, 1315, 1294, 1236, 1187, 1123, 1073, 1024, 999, 875, 852, 752, 728, 702, 635, 577, 563, 522, 491, 467 cm⁻¹. EI-MS (70 eV): m/z = 558[M⁺]. Anal. Calcd for C₂₆H₃₀Cl₂O₂PSV: C, 55.82; H, 5.41. Found: C, 55.78; H, 5.37.

Complex 2b

Yield: 54%. IR (KBr pellets): ν 3387, 3121, 2787, 1698, 1654, 1534, 1521, 1487, 1468, 1432, 1389, 1221, 1165, 1034, 998, 945, 876, 745, 653, 632, 559, 524, 498, 477, 453 cm⁻¹. EI-MS (70 eV): m/z = 630[M⁺]. Anal. Calcd for C₂₉H₃₈Cl₂O₂PSSiV: C, 55.15; H, 6.06. Found: C, 55.11; H, 6.12.

Characterization of the Polymers

The NMR data of PEs and ethylene/1-hexene copolymers were obtained on a Bruker 400 MHz spectrometer at 135 °C with *o*-C₆D₄Cl₂ as a solvent. DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 K/min. The weight-average molecular weight (M_w) and the polydispersity

index (PDI) of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 µm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

Ethylene Polymerization

Ethylene polymerization was carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. Appropriate toluene was introduced into the nitrogen-purged reactor and stirred vigorously (600 r/min). The toluene was kept at a prescribed polymerization temperature, and then ethylene gas feed was started. After 15 min, a solution of Et_2AlCl in toluene and a solution of ETA in toluene were added and stirred for 5 min. Then a toluene solution of the vanadium complexes was added into the reactor with vigorous stirring (900 r/min) to initiate polymerization. Total volume of the reaction solution was kept in 50 mL. After a prescribed time, acidic alcohol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulting mixture was added to acidic alcohol. The solid polyethylene was isolated by filtration, washed with alcohol, and dried at 60 °C for 24 h in a vacuum oven.

Ethylene/1-Hexene Copolymerization

Copolymerization was carried out in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. The reactor was charged with 20 mL of toluene and the prescribed amount of 1-hexene. Next, the ethylene gas feed was started followed by equilibration at the desired polymerization temperature. After 15 min, a solution of Et_2AlCl in toluene and a solution of ETA in toluene were added and stirred for 5 min. Subsequently, a toluene solution of vanadium complexes was added into the reactor with vigorous stirring (900 r/min) to initiate polymerization. Total volume of the reaction solution was kept in 30 mL. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulting mixture was added to acidic ethanol. The polymer was isolated by filtration, washed with ethanol and dried at 60 °C for 12 h in a vacuum oven.

RESULTS AND DISCUSSION

Synthesis and Characterization of Vanadium(III) Complexes

Previously, we had synthesized a series of bidentate [O,P] and [O,P=O] vanadium complexes. In this work, we picked out two complexes possessing similar structure with [S,P] complexes from each group for comparing, as shown in Fig. 1. A general synthetic route for [S,P] vanadium complexes used in this study is shown in Fig. 2. The reaction of $\text{VCl}_3(\text{THF})_3$ with 1.0 equiv of ligand in tetrahydrofuran (THF) in the presence of excess TEA afforded vanadium(III) complexes in moderate yields. These reactions took place along with evolution of hydrochloride, and the pure samples as yellow green crystallized solids were isolated from the chilled concentrated mixture of THF and hexane solution. They were identified by FTIR and mass spectra as well as elemental analysis. The resonances are broadened to such an extent that they become effectively unobservable in the ^1H -NMR spectra for these complexes in CD_2Cl_2 or C_6D_6 , indicating that they are paramagnetic species.

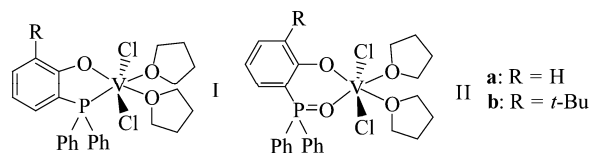


Fig. 1 Previously reported [O,P] and [O,P=O] vanadium(III) complexes

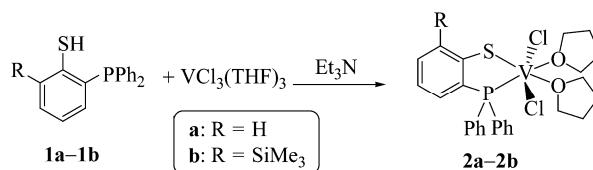


Fig. 2 General synthetic route of the vanadium complexes used in this study

The FTIR spectra of **1a** and **2a** were studied, and the results are presented in Fig. 3. It clearly indicated the disappearance of a sharp peak representing stretching frequencies of S—H at about 2550 cm⁻¹. Instead, stretching frequencies of tetrahydrofuran at about 3411, 3058, and 2965 cm⁻¹ were observed. In addition, the strong band of ν(P-Ph) at around 1178 cm⁻¹ shifted to lower frequency around 1123 cm⁻¹. The proposed structure is in line with the elemental analysis. A little different from **1a**, a broad peak representing stretching frequencies of OH at about 3000 cm⁻¹ in [O,P] and [O,P=O] ligands was observed. Like the comparison of **1a** and **2a**, a similar difference in FTIR spectra was observed for **1b** and **2b**.

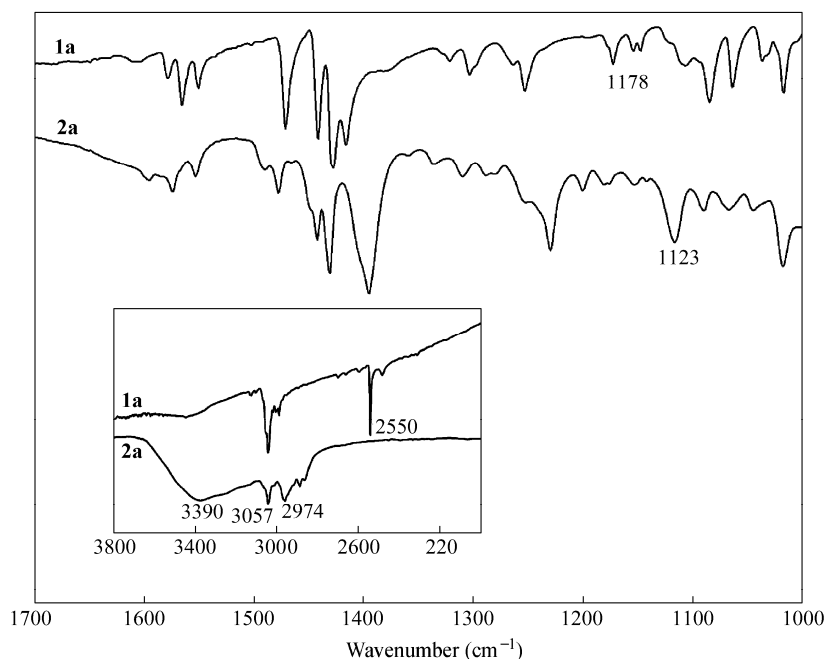


Fig. 3 IR spectra of ligand **1a** and complex **2a**

Ethylene Polymerization

Co-catalysts, especially alkylaluminiums, play an irreplaceable role in the olefin polymerization promoted by vanadium catalysts, and the performance of catalysts depends considerably on the nature of the co-catalyst. Et₂AlCl was proved to be an efficient cocatalyst in the [O,P] and [O,P=O] vanadium catalytic systems, thus we chose it as the cocatalyst and optimized reaction conditions with complexes **2a** and **2b**. Cl₃CCOOEt (ETA) was used as a reactivating agent to reactivate the low-valent, less active or inactive species to active vanadium(III) species. The typical results of the polymerization are collected in Table 1 and Fig. 4. Note that all [S,P] catalysts are highly active toward ethylene polymerization even at high reaction temperatures, and the highest activity (26.2 kg PE/(mmol·h)) was obtained by catalyst **2a** at 50 °C. The activities of the two catalysts were increased first and then gradually decreased with the increase of temperature, and usually obtained the highest activity at 50 °C. The activities of all [S,P] catalysts were no significant fall even at 70 °C, indicating the potential high thermal stability.

Table 1. Typical results of ethylene polymerization by complexes **2a–2b**^a

Entry	Cat.	Temp (°C)	Catalyst (μmol)	Time (min)	Polymer (g)	Activity ^b	M_w^c (kg/mol)	M_w/M_n^c
1	2a	50	0.5	5	1.09	26.2	44.0	2.8
2	2b	50	0.5	5	1.06	25.4	49.7	2.7
3	2b	70	0.2	5	0.31	18.6	34.0	2.3
4	2b	70	0.2	15	0.71	14.2	37.0	2.8
5	2b	70	0.2	30	0.98	9.80	41.0	2.3
6	2b ^d	50	0.5	5	0.41	9.84	196	2.7
7	2b ^e	50	0.5	5	0.56	13.4	127	2.4

^a Reaction conditions: 0.1 MPa of ethylene pressure, $\text{Cl}_3\text{CCO}_2\text{Et}/\text{V}$ (molar ratio) = 300, Al/V (molar ratio) = 4000, toluene 50 mL; ^b kg/mmole·h; ^c Determined by GPC in 1,2,4-trichlorobenzene versus polystyrene standard; ^d Al/V (molar ratio) = 500; ^e Al/V (molar ratio) = 2000

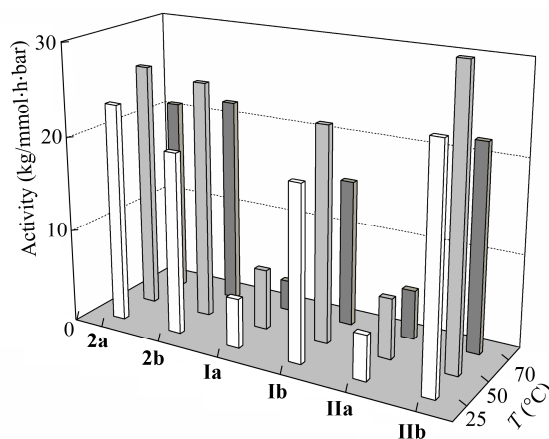


Fig. 4 Catalytic activities of vanadium complexes toward ethylene polymerization at different temperatures. Reaction conditions: 0.5 μmol of vanadium complex, $\text{Cl}_3\text{CCO}_2\text{Et}$ 0.15 mmol, Et_2AlCl 2 mmol, ethylene 0.1 MPa, toluene 50 mL, polymerization for 5 min

Except temperature, substituents in the ligands also greatly influence catalytic activities, as shown in Fig. 4. **1a–1b** and **11a–11b** were also tested for ethylene polymerization under the same condition for comparison. Complex **1a** and **11a** (without any substituents) displays relatively low catalytic activity, indicating that weak steric effect may be helpless for improving catalyst performance. In contrast to low activities of **1a** and **11a**, **1b** and **11b**, with *t*-Bu group on the ortho-position of the benzene ring, show much higher activities, indicating that proper steric hindrance on the ligand may avoid active species deactivating in some extent. However, for [S,P] vanadium catalysts, **2a** (without substituents) shows much higher activity than **1a** and **11a**, which may be attributed to benefits of introduction of second-row donor atoms for adjusting charge density of the vanadium centers. This result further proves the soft donor effect is beneficial to catalyst performance. Although **2b** possessed trimethylsilyl groups with large steric hindrance, it exhibited high activities, almost the same as **2a** under the same condition.

The effect of reaction conditions on the ethylene polymerization was investigated by using catalyst **2b**. The increase in Et_2AlCl concentration resulted in an increase in catalytic activity but a decrease in the molecular weight of polyethylenes (entries 2, 6 and 7 in Table 1) which suggested the existence of chain transfer to Al reactions. The ^{13}C - and ^1H -NMR spectra revealed that the signals belonging to chain-end double bonds were not detected for low molecular weight copolymers, also indicating that chain transfer to aluminium was the dominant chain-transfer pathway under these reaction conditions. All the polymers prepared were linear polyethylene confirmed by ^{13}C -NMR spectra, which is similar to that for β -enaminoketonato or salicylaldiminato vanadium catalysts reported previously^[39, 40].

In addition, we have studied the relationship between the catalytic activity and polymerization time using

2b. Ethylene polymerization lifetime studies at 70 °C and at 15 and 30 min were conducted for verifying their deactivation process (entries 3, 4 and 5 in Table 1). It was found that there was a gradual decline in catalytic activities, indicating that [S,P] catalysts retain a high degree of activity even under high temperature and long polymerization time.

Ethylene/1-Hexene Copolymerization

In order to further evaluate the performance of these catalysts, we studied the copolymerization of ethylene/1-hexene, and the representative results are summarized in Table 2. According to ethylene polymerization results, we also studied **I** and **II** in the copolymerization of ethylene/1-hexene for comparison. Catalytic activity and 1-hexene incorporation in the copolymer are important indicators for evaluating performance. **2a–2b**, bearing soft phosphorus and sulfur atom, displayed excellent performance from the aspects of catalytic activities and 1-hexene incorporation. Especially **2a**, displays the second highest activities in ethylene/1-hexene copolymerization after **IIa** and the highest 1-hexene incorporation among all the catalysts. This result tells us that soft phosphorus and sulfur atoms coordinating with vanadium simultaneously not only adjust charge density of the vanadium centers but also avoid possible deactivation reaction. This study provides us a new way for designing high-performance catalysts.

Table 2. Copolymerization of ethylene and 1-hexene by vanadium complexes ^a

Entry	Cat.	Temp (°C)	1-Hexene (mol/L)	Polymer (g)	Activity ^b	Incorp ^c	M_w ^d (kg/mol)	M_w/M_n ^d	T_m (°C) ^e
1	2a	25	0.2	0.78	4.68	3.97	51.2	2.2	116.1
2	2b	25	0.2	0.74	4.44	3.48	63.7	1.7	115.7
3	Ia	25	0.2	0.14	0.84	3.75	41.1	2.2	109.3
4	Ib	25	0.2	0.65	3.90	3.57	52.1	1.8	114.1
5	IIa	25	0.2	0.21	1.26	3.88	46.7	2.7	108.6
6	IIb	25	0.2	0.89	5.34	3.80	44.3	2.1	116.3
7	2a	25	0.5	0.41	2.46	6.62	27.4	2.4	103.5
8	2a	25	1.0	0.21	1.26	14.7	12.6	2.1	—
9	2a	50	0.2	1.09	6.54	4.25	33.2	3.8	110.3
10	2a	70	0.2	0.74	4.44	4.83	17.4	4.2	108.2
11	2a ^f	25	0.2	0.43	2.58	3.81	86.7	2.9	116.5
12	2a ^g	25	0.2	0.69	4.14	3.87	68.4	2.6	117.1
13	IIb	25	0.5	0.46	2.76	6.45	24.8	1.8	104.5
14	IIb	25	1.0	0.22	1.32	11.4	13.6	2.3	—

^a Conditions: toluene + comonomer = 30 mL, ethylene 0.1 MPa, catalyst 1.0 μ mol, cocatalyst Et₂AlCl 4.0 mmol, ETA/V = 300 (molar ratio), 10 min; ^b Activity in kg of polymer/(mmol_V·h); ^c Comonomer content (mol%) estimated by ¹³C-NMR spectra; ^d GPC data in 1,2,4-trichlorobenzene versus polystyrene standard; ^e Determined by DSC; ^f Al/V (molar ratio) = 500; ^g Al/V (molar ratio) = 2000

The effect of reaction conditions on the copolymerization of ethylene/1-hexene was also investigated by using catalyst **2a**. The copolymerization was sensitive to reaction temperature. As shown in entries 1, 9–10 (Table 2), an enhancement in reaction temperature from 25 °C to 70 °C led to an increase in 1-hexene incorporation (from 3.97% to 4.83%), but a decrease in the molecular weight of the resultant copolymer, while the molecular weight distribution of the copolymers almost remained constant. Then, the increase of initial hexane concentration led to an increase in the 1-hexene incorporation, while catalytic activity, the melting temperature and the M_w of the resultant polymers gradually decreased (entries 1, 7–8). Finally, a dependence of catalytic activity on Et₂AlCl concentration is observed. As shown in entries 1, 11, 12 (Table 2), a maximal activity of 4.68 kg/(mmol_V·h) is obtained when the Al/V (molar ratio) equals 4000, whereas the molecular weight of the resultant polymers decreases with the increase of Al/V (molar ratio) from 500 to 4000, indicating the chain transfer reaction to Al occurs. But the 1-hexene incorporation of the copolymer remains fairly static with the increase of Et₂AlCl concentration. In addition, the molecular weight distributions remains constant, indicating a single-site catalytic behavior.

The microstructures of ethylene/1-hexene copolymers are established by ^{13}C -NMR in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at $135\text{ }^\circ\text{C}$, with the assignment of the microstructure following the previous work reported by Hsieh and Randall^[41, 42]. We selected **2a** and **IIb** for in-depth research. As shown in Fig. 5, 1-hexene incorporation of the polymer obtained by **2a** (14.7 mol%) was much higher than that by **IIb** (11.4 mol%) when concentration of 1-hexene reached 1.0 mol/L, although the activity of **2a** was a little lower than that of **IIb**. Besides, the resultant copolymer by **2a** possessed a kind of inverse insertion unit (assigned as $S_{\alpha\beta}$), but no existence for that by **IIb**. We want to know if such difference only appears when 1-hexene incorporation of the copolymer was high. Turn down the concentration of 1-hexene to 0.5 mol/L, as shown in Fig. 5, the resultant copolymer obtained by **2a** also possessed the unit of $S_{\alpha\beta}$ and $S_{\beta\beta}$ (alternating sequence), but no existence for **IIb**, although 1-hexene incorporations for them get pretty close to each other. Despite the differences listed above, the microstructures of the polymers obtained by **2a** and **IIb** had a lot in common. Isolated 1-hexene inserted unit ([EHE] assigned as $T_{\delta\delta}$) among the repeated ethylene insertions is the most abundant composition in polymer chains; the signals at δ 28.0 ($S_{\beta\gamma}$) and 38.9 ($T_{\gamma\delta}$) caused by the inverse insertion sequences of 1-hexene were both found in the spectra for **2a** and **IIb**; other weak signals can be assigned as one or a few ethylene units arranged between two 1-hexene units. The possible monomer sequences in the copolymer are summarized in Fig. 6.

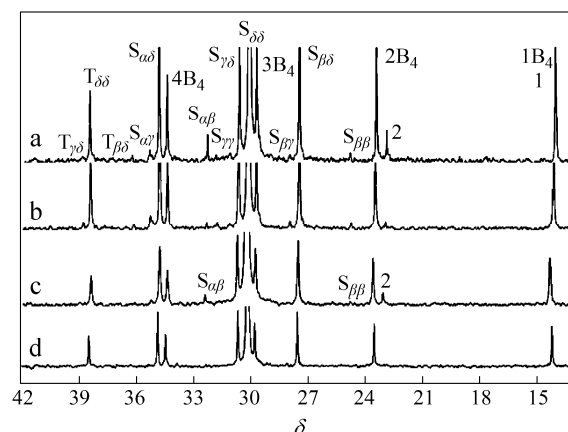


Fig. 5 ^{13}C -NMR of ethylene/1-hexene copolymers using catalyst: (a) **2a** 14.7 mol% (entry 8), (b) **IIb** 11.4 mol% (entry 14), (c) **2a** 6.62 mol% (entry 7) and (d) **IIb** 6.45 mol% (entry 13)

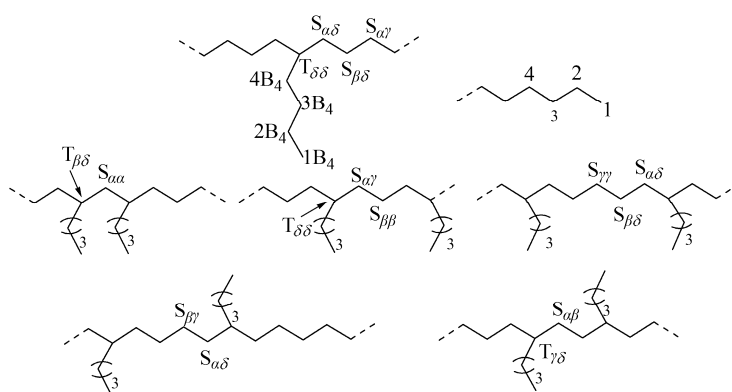


Fig. 6 Possible monomer sequences in poly(ethylene-co-hexene)s

The triad distribution data and reactivity ratios r_E and r_H for each catalyst were calculated at $50\text{ }^\circ\text{C}$ according to ^{13}C -NMR results using the method of Hsieh and Randall^[41, 42]. The steric hindrance and electron effect of the ligands exerted obvious influence on the value of r_E and r_H , which manifested as the capability of

incorporation of 1-hexene. Generally speaking, the change in r_E (from 28.78 to 44.30) is in turn more remarkable than r_H (from 0.140 to 0.175), indicating the change of substituent group has more significant impact on ethylene insertion. As shown in Table 3, the r_E value of **2a** is much smaller than that of the other catalysts, indicating their good capabilities for copolymerization. Complex **2b** ($r_E = 42.06$; $r_H = 0.175$) showed higher tendency to incorporate 1-hexene than **1b** ($r_E = 44.30$; $r_H = 0.140$), indicating that [S,P] catalysts show good performance from the aspect of catalytic activity and 1-hexene incorporation, which is consistent with the results at 25 °C. These results indicate that the conclusions on reactivity ratios and 1-hexene incorporation calculated from ^{13}C -NMR are unanimous.

Table 3. Triad distributions and reactivity ratios for ethylene/1-hexene copolymerization

Cat.	$[\text{H}]_{\text{feed}}$	$[\text{H}]_{\text{copolymer}}$	[EHE]	[EHH]	[HHH]	[HEH]	[HEE]	[EEE]	r_E	r_H
2a	0.677	0.057	0.033	0.020	0	0	0.093	0.854	28.78	0.141
2b	0.677	0.042	0.024	0.017	0	0	0.066	0.893	42.06	0.175
1b	0.677	0.038	0.025	0.013	0	0	0.063	0.899	44.30	0.140

CONCLUSIONS

In summary, we have prepared and characterized a series of vanadium(III) complexes bearing [S,P] ligands (**2a–2b**). The complexes displayed high catalytic activity toward ethylene polymerization in the presence of Et_2AlCl as a cocatalyst and Cl_3CCOOEt as a reactivating agent and produced high molecular weight polyethylenes with unimodal MWD even at elevated reaction temperatures. This result further proves the soft donor effect is beneficial to catalyst performance. In addition, these complexes with optimized structure also exhibited high catalytic activity for ethylene/1-hexene copolymerization. To further investigate the copolymerization system, the reactivity ratios of comonomers were determined using ^{13}C -NMR methods of Hsieh and Randall. The steric hindrance and electronic effect of the ligands exert obvious influence on the values of r_E and r_H , which manifest the copolymerization capability of catalysts.

REFERENCES

- Coates, G.W., *Chem. Rev.*, 2000, 100(4): 1223
- Gibson, V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, 103(1): 283
- Domski, G.J., Rose, J.M., Coates G.W., Bolig, A.D. and Brookhart, M., *Prog. Polym. Sci.*, 2007, 32(1): 30
- Matsugi, T. and Fujita, T., *Chem. Soc. Rev.*, 2008, 37: 1264
- Stelzig, S.H., Tamm, M. and Waymouth, R.M., *J. Polym. Sci. Part A: Polym. Chem.*, 2009, 47(22): 6064
- Natta, G., Pasquon, I. and Zambelli, A., *J. Am. Chem. Soc.*, 1962, 84(8): 1488
- Carrick, W.L., *J. Am. Chem. Soc.*, 1958, 80(23): 6455
- Carrick, W.L., Kluiber, R.W., Bonner, E.F., Wartman, L.H., Rugg, F.M. and Smith, J.J., *J. Am. Chem. Soc.*, 1960, 82(15): 3883
- Lehr, M.H. and Carmen, C.J., *Macromolecules*, 1969, 2(2): 217
- Lehr, M.H., *Macromolecules*, 1968, 1(2): 178
- Zambelli, A., Pasquon I., Signorini, R. and Natta, G., *Makromol. Chem.*, 1968, 112: 160
- Doi, Y., Kinoshita, J., Morinaga, A. and Keii, T., *J. Polym. Sci. Polym. Chem. Ed.*, 1975, 13(11): 2491
- Christman, D.L. and Keim, G.I., *Macromolecules*, 1968, 1(4): 358
- Doi, Y., Suzuki, S. and Soga, K., *Macromolecules*, 1986, 19(12): 2896
- Addisson, E., *J. Polym. Sci. Part A: Polym. Chem.*, 1994, 32(6): 1033
- Gambarotta, S., *Coord. Chem. Rev.*, 2003, 237(1-2): 229
- Hagen, H., Boersma, J. and van Koten, G., *Chem. Soc. Rev.*, 2002, 31: 357
- Redshaw, C., *Dalton Trans.*, 2010, 39(24): 5595

- 19 Nomura, K. and Zhang, S., *Chem. Rev.*, 2011, 111(3): 2342
- 20 Wu, J.Q. and Li, Y.S., *Coord. Chem. Rev.*, 2011, 255(19-20): 2303
- 21 Wu, J.Q., Li, Y.G., Li, B.X. and Li, Y.S., *Chinese J. Polym. Sci.*, 2011, 29(5) : 627
- 22 Jiang, T., Chen, H.X., Cao, C.G., Mao, G.L., Du, W. and Wang, D.F., *Chinese J. Polym. Sci.*, 2011, 29(4): 475
- 23 Redshaw, C., Warford, L., Dale, S.H. and Elsegood, M., *Chem. Commun.*, 2004; 1954
- 24 Redshaw, C., Rowan, M.A., Homden, D.M., Dale, S.H., Elsegood, M., Matsui, S. and Matsuura, S. *Chem. Commun.*, 2006, 3329
- 25 Redshaw, C., Rowan, M.A., Warford, L., Homden, D.M., Arbaoui, A., Elsegood, M., Dale, S.H., Yamato, T., Casas, C.P., Matsui, S. and Matsuura, S., *Chem. Eur. J.*, 2007; 13(4): 1090
- 26 Nomura, K., Sagara, A. and Imanishi, Y., *Macromolecules*, 2002, 35(5): 1583
- 27 Yamada, J., Yamada, J. and Nomura, K., *Organometallics*, 2005, 24(10): 2248
- 28 Fujiki, M. and Nomura, K., *Organometallics*, 2005, 24(15): 3621
- 29 Wang, W. and Nomura, K., *Macromolecules*, 2005, 38(14): 5905
- 30 Wang, W. and Nomura, K., *Adv. Synth. Catal.*, 2006, 348(6): 743
- 31 Nomura, K., Atsumi, T., Fujiki, M. and Yamada, J., *J. Mol. Catal. A: Chem.*, 2007, 275(1-2): 1
- 32 Wu, J.Q., Mu, J.S., Zhang, S.W. and Li, Y.S., *J. Polym. Sci. Part A: Polym. Chem.*, 2010, 48(5): 1122
- 33 Long, R.J., Gibson, V.C. and White, A.J.P., *Organometallics*, 2008, 27(2): 235
- 34 Long, R.J., Jones, D.J. and Gibson, V.C., *Inorg. Chem.*, 2006, 45(2): 511
- 35 Long, R.J., Jones D.J. and Gibson, V.C., *Organometallics*, 2008, 27(22): 5960
- 36 Zhang, S.W., Lu, L.P., Li, B.X. and Li, Y.S., *J. Polym. Sci. Part A: Polym. Chem.*, 2012, 50(22): 4721
- 37 He, L.P., Mu, H.L., Li, B.X. and Li, Y.S., *J. Polym. Sci. Part A: Polym. Chem.*, 2010, 48(2): 311
- 38 He, L.P., Liu, J.Y., Li, Y.G., Liu, S.R. and Li, Y.S., *Macromolecules*, 2009, 42(21): 8566
- 39 Wu, J.Q., Pan, L., Hu, N.H. and Li, Y.S., *Organometallics*, 2008, 27(15): 3840
- 40 Tang, L.M., Wu, J.Q., Duan, Y.Q., Pan, L., Li, Y.G. and Li, Y.S., *J. Polym. Sci. Part A: Polym. Chem.*, 2008, 46(6): 2038
- 41 Reybuck, S.E., Meyer, A. and Waymouth, R.M., *Macromolecules*, 2002, 35(3): 637
- 42 Hsieh, E.T. and Randall, J.C., *Macromolecules*, 1982, 15(5): 1402