Ethylene Polymerization and Ethylene/Hexene Copolymerization with Vanadium(III) Catalysts Bearing Heteroatom-Containing Salicylaldiminato Ligands

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ABSTRACT: A series of novel vanadium(III) complexes bearing heteroatom-containing group-substituted salicylaldiminato ligands [RN=CH(ArO)]$VCl_2(THF)_2$ (Ar = C_6H_4, R = C_3H_2NS, **2a**; C_7H_4NS, **2c**; $C_7H_5N_2$, **2d**; Ar = $C_6H_2tBu_2$ (2,4), R = C_3H_2NS, **2b**) have been synthesized and characterized. Structure of complex **2c** was further confirmed by X-ray crystallographic analysis. The complexes were investigated as the catalysts for ethylene polymerization in the presence of Et_2AlCl. Complexes **2a–d** exhibited high catalytic activities (up to 22.8 kg polyethylene/$mmol_V$ h bar), and affording polymer with unimodal molecular weight distributions at 25–70 °C in the first 5-min polymerization, whereas produced bimodal molecular weight distribution polymers at 70 °C when polymerization time prolonged to 30 min. The catalyst structure plays an important role in controlling the molecular weight and molecular weight distribution of the resultant polymers produced in 30 min polymerization. In addition, ethylene/hexene copolymerizations with catalysts **2a–d** were also explored in the presence of Et_2AlCl, which leads to the high molecular weight and unimodal distributions copolymers with high comonomer incorporation. Catalytic activity, comonomer incorporation, and polymer molecular weight can be controlled over a wide range by the variation of catalyst structure and the reaction parameters, such as comonomer feed concentration, polymerization time, and polymerization reaction temperature. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 3573–3582, 2009

Keywords: catalysts; copolymerization; Ziegler-Natta polymerization

INTRODUCTION

Since the 1950s, vanadium catalysts have played a critically important role in producing high-molecular-weight polyethylene (PE) with narrow molecular weight distribution as well as α-olefin or cycloolefin copolymers with high comonomer incorporations.[1,2] One of the key issues concerning widely investigated vanadium-based olefin polymerization catalysts is the loss of productivity at elevated temperatures. It is apparent from past decades studies that the predominant cause of this phenomenon is ascribed to reduction of catalytically active vanadium species to low-valent, less active, or inactive species.[3,4] Design and

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Additional Supporting Information may be found in the online version of this article.

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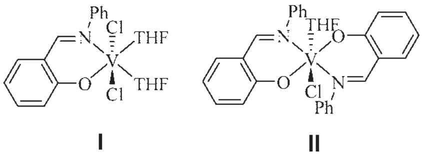


Scheme 1. Previously reported catalysts.

synthesize ancillary ligands to stabilize the active species has proved to be an effective approach.[5–25] A series of thermal robust vanadium catalysts have been reported recently, for example, the bis (benzimidazole) amine vanadium catalysts reported by Gibson's group displayed high efficiency for ethylene (co)polymerization and showed remarkable thermal stability.[5(c)] Aryloxide-based vanadyl complexes, reported by Redshaw's group, exhibited excellent performance in olefin polymerization at an elevated temperature.[17] High-valent imido vanadium(IV or V) complexes were also tested as promising catalysts for ethylene (co) polymerization at an ambient temperature.[15–17] The immobilization of soluble vanadium olefin polymerization catalysts onto inorganic supports (SiO_2, $MgCl_2$, MgO, etc.) is an another effective method to enhance the chemical stability of the catalyst species.[22]

Recently, we have introduced a series of bidentate salicylaldiminato ligands to coordinate with vanadium(III) (Scheme 1), and they have been found to be efficient catalysts for ethylene polymerization in the presence of Et_2AlCl and $Cl_3CCOOEt$. However, the fast deactivation or chain transfer to aluminum took place, and broad molecular weight distribution polymers were obtained at an elevated polymerization temperature by the monosalicyladiminato vanadium(III) complexes.[26(a)] Heteroatom-containing group-substituted ancillary ligands supporting group IV complexes have been applied as effective catalysts for ethylene (co)polymerization.[27] This work was initially aimed at introducing a variety of heteroatoms containing groups such as thiazole, benzothiazole, and benzimidazole to the *N*-aryl of the salicylaldiminato ligands, which were used as bidentate ligands to stabilize vanadium(III) complexes. These complexes as catalysts for ethylene (co)polymerization were investigated in detail.

EXPERIMENTAL

General Procedures and Materials

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 300 MHz spectrometer at an ambient temperature, with $CDCl_3$ as the 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). The NMR data of PE and ethylene/1-hexene copolymers were obtained on a Varian Unity-400 MHz spectrometer at 135 °C with o-$C_6D_4Cl_2$ as a solvent. The DSC measurements were performed on a Perkin–Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/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 used as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The intrinsic viscosity of the polymer sample was measured in decalin at 135 °C using an Ubbleohed viscometer, and the viscosity–average molecular weight was calculated using the following equation.[28]

$$[\eta] = 6.2 \times 10^{-4} {M_v}^{0.7}$$

Ethyl trichloroacetate (ETA) were purchased from Aldrich, dried over calcium hydride at a room temperature, and then distilled. The *n*-butyllithium solution in hexane and $VCl_3(THF)_3$ was purchased from Aldrich. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical. Diethylaluminium chloride (DEAC) was obtained from Albemarle Corp. The ligands used were synthesized according to the literature methods.[29]

Synthesis of Vanadium Complexes

$[C_3H_2NSN{=}CH(C_6H_4O)]VCl_2(THF)_2$ (2a)

To a stirred solution of $VCl_3(THF)_3$ (0.37 g, 1.0 mmol) in dried tetrahydrofuran (THF, 20 mL) was added slowly a solution of 2-($C_3H_2NSN{=}CH$)C_6H_4OH (**1a**, 0.20 g, 1.0 mmol) in THF (20 mL). The red reaction mixture was stirred for 10 min and Et_3N (0.15 mL, 108 mg, 1.05 mmol) was added. After stirring for 4 h at room temperature, the solution was concentrated to about 10 mL, and then the mixture was filtered to remove NH_4Cl. Crystallization by diffusion of *n*-hexane (5 mL) into the clear solution yielded red crystals of **2a** (0.27 g, 58%). Complexes **2b–d** were prepared analogously. IR (KBr pellets): ν 3104, 2973, 1605, 1576, 1535, 1513, 1430, 1377, 1301, 1193, 1150, 1127, 921, 865, 762, 566, 447 cm^{-1}. EI-MS (70ev): $m/z = 467$ [M^+]. Anal. calcd. for $C_{18}H_{21}Cl_2N_2O_3SV$: C, 46.27; H, 4.53; N, 5.99. Found: C, 46.39; H, 4.58, N, 6.03.

$[C_3H_2NSN{=}CH(OC_6H_2tBu_2\text{-}2,4)]VCl_2(THF)_2$ (2b)

Yield: 65%. IR (KBr pellets): ν 3115, 2958, 2869, 1608, 1573, 1537, 1512, 1434, 1362, 1318, 1254, 1178, 1132, 848, 748, 544 cm^{-1}. EI-MS (70ev): $m/z = 579$ [M^+]. Anal. calcd. for $C_{26}H_{37}Cl_2N_2O_3SV$: C, 53.89; H, 6.44; N, 4.83. Found: C, 53.94; H, 6.40, N, 4.78.

$[C_7H_4NSN{=}CH(C_6H_4O)]VCl_2(THF)_2$ (2c)

Yield: 45%. IR (KBr pellets): ν 3055, 2973, 2874, 1604, 1571, 1536, 1464, 1428, 1377, 1296, 1184, 1142, 1065, 1012, 875, 837, 759, 673, 615, 517, 440 cm^{-1}. EI-MS (70ev): $m/z = 517$ [M^+]. Anal. calcd. for $C_{22}H_{23}Cl_2N_2O_3SV$: C, 51.08; H, 4.48; N, 5.41. Found: C, 51.21; H, 4.39, N, 5.43.

$[C_7H_5N_2N{=}CH(C_6H_4O)]VCl_2(THF)_2$ (2d)

Yield: 48%. IR (KBr pellets): ν 3056, 2927, 2684, 1606, 1580, 1535, 1444, 1391, 1308, 1278, 1203, 1149, 927, 823, 741, 608, 521 cm^{-1}. EI-MS (70ev): $m/z = 500$ [M^+]. Anal. calcd. for $C_{22}H_{24}Cl_2N_3O_3V$: C, 52.82; H, 4.84; N, 8.40. Found: C, 52.96; H, 4.78, N, 8.34.

Ethylene Polymerization

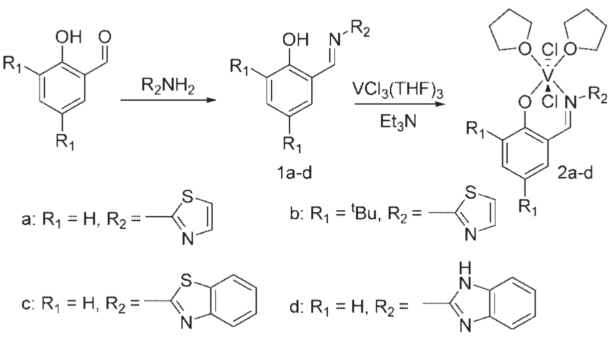
Polymerization was carried out under atmospheric pressure in toluene in a 150-mL glass reactor equipped with a mechanical stirrer. Toluene (45 mL) was introduced into the nitrogen-purged reactor and stirred vigorously (300 rpm). The toluene was kept at a prescribed polymerization temperature, and then 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, and then a toluene solution of the catalyst was added into the reactor with vigorous stirring (600 rpm) to initiate polymerization. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulted mixture was added to acidic ethanol. The solid PE was isolated by filtration, washed with methanol, and dried at 60 °C for 24 h in a vacuum oven.

Ethylene/Hexene Copolymerization

Copolymerization was also carried out under atmospheric pressure 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, the ethylene gas feed was started followed by equilibration at 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 (600 rpm) to initiate polymerization. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulted 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.

Crystallographic Studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. The intensity data were collected with the ω scan mode (186 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz, polarization factors were made for the intensity data, and absorption corrections were performed using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares method. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Crystal data for **2c**: $C_{26}H_{33}Cl_2N_2O_4SV$, $M_r = 591.44$, monoclinic, space group P2(1)/c, red crystal $0.42 \times 0.32 \times 0.12$ mm^3, $a = 17.0933(12)$, $b = 8.1580(6)$, $c = 21.0246(15)$, $\alpha = 90.00°$, $\beta = 110.1280(10)°$, $\gamma = 90.00°$, $V = 2752.8(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.427$, $2.98° < \theta < 25.81°$, 8028 reflections measured, 5381 unique ($R_{int} = 0.0185$), which were used in all



Scheme 2. Synthesis of the vanadium complexes **2a–d**.

calculations. The final $wR_2 = 0.0928$ (all data), $R_1 = 0.0376$, and GOF = 1.037.

RESULTS AND DISCUSSION

Synthesis and Characterization of Bidentate Salicyladiminato Vanadium(III) Complexes

A general synthetic route for new vanadium complexes (**2a–d**) is shown in Scheme 2. The reaction of $VCl_3(THF)_3$ with 1.0 equivalent (RN=CH)-ArOH (**1a–d**) in THF in the presence of excessive Et_3N afforded vanadium(III) complexes **2a–d** in moderate yields (**2a**, 58%; **2b**, 65%; **2c**, 45%; **2d**, 48%). These reactions took place along with the evolution of hydrochloride, and the pure samples as dark red or brown crystallized solids were isolated from the chilled concentrated mixture of THF and hexane solution. These complexes were identified by FTIR and mass spectra as well as elemental analysis. As the previous reported salicyladiminato vanadium(III) complexes,[26] these complexes were also paramagnetic, which were silent to NMR.

The crystal of complex **2c** suitable for X-ray structure determination was grown from THF–hexane solution. The molecule structure is shown in Figure 1. In solid state, it folds a six coordinate distorted octahedral geometry around the V metal center. The N, S atoms on benzothiazole group are not coordinated to vanadium because of the distorted strain. The two chlorine atoms are situated in the trans position, whereas two THF molecules are in the cis position to each other, as seen in the bond angles for Cl(1)—V—Cl(2) (174.28°) and O(2)—V—O(3) (86.43°). These bond angles are somewhat analogous to those in vanadium complex $[PhN{=}CH(C_6H_4O)]VCl_2(THF)_2$ [Cl(1)—V—Cl(2) (174.75°) and O(2)—V—O(3) (89.71°)], reported previously.[26] The V—Cl bonds bond distances (2.3713, 2.3473 Å) are also close to those of the values reported.[26,30]

Ethylene Polymerizations

Complexes **2a–d** have been investigated as the effective catalysts for ethylene polymerization in the presence of Et_2AlCl and $Cl_3CCOOEt$ under atmospheric pressure. As shown in Table 1, ligand structure and reaction temperature considerably influence catalytic activities and the molecular weights of the polymers obtained. With the introduction of heteroatom-containing group onto the *N*-aryl moiety of the ligands, these complexes exhibited higher catalytic activities toward ethylene polymerization at an elevated polymerization temperature (70 °C) than complex **I**, although they only showed much lower activities at an ambient temperature compared with **I**. Complex **2c** displayed the highest catalytic activity (22.8 kg/mmol$_V$ h bar) among four complexes at 50 °C. Complex **2b** bearing bulky *tert*-butyl on the aryloxy moiety of the ligand showed much lower catalytic activities than complex **2a**, indicating that the steric effect of the aryloxy moiety of the ligand would suppress chain propagation reaction to some content. Compared with complex **2a**, complex **2c** displayed comparable activities. Noticeably, the catalytic activities of complex **2c** are much higher than those of complex **2d** under the same conditions, suggesting that the electronic effect of the *N*-aryl moiety of the salicyladiminato ligands directly influences vanadium catalyst's performance. Although the molecular weights of the polymers obtained by vanadium complexes

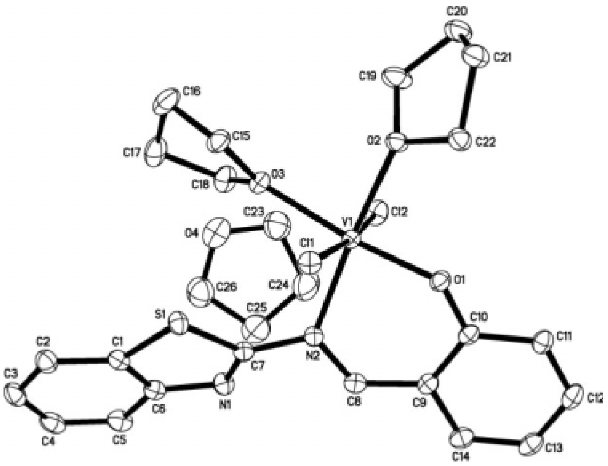


Figure 1. Molecular structure of complex **2c**. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1. Ethylene Polymerization by Catalysts **2a–d**[a]

Entry	Catalyst (μmol)	t (min)	T (°C)	Polymer (g)	Activity[b]	M_w[c] ($\times 10^3$)	M_w/M_n[c]
1	**2a** (0.5)	5	25	0.65	15.6	89.5	2.19
2	**2a** (0.5)	5	50	0.68	16.3	20.5	2.56
3	**2a** (0.5)	5	70	0.72	17.3	11.0	2.09
4	**2a** (0.1)	30	70	0.38	7.6	407[d]	20.64
5	**2b** (0.5)	5	25	0.37	8.9	94.2	2.16
6	**2b** (0.5)	5	50	0.59	14.2	27.8	2.44
7	**2b** (0.5)	5	70	0.60	14.4	11.9	2.80
8	**2b** (0.1)	30	70	0.13	2.6	110[d]	11.67
9	**2c** (0.5)	5	25	0.58	13.9	95.6	2.28
10	**2c** (0.5)	5	50	0.95	22.8	26.8	2.27
11	**2c** (0.5)	5	70	0.76	18.2	13.0	2.34
12	**2c** (0.1)	30	70	0.43	8.6	721[d]	26.5
13	**2d** (0.5)	5	25	0.26	6.2	116	2.53
14	**2d** (0.5)	5	50	0.54	13.0	27.1	2.39
15	**2d** (0.5)	5	70	0.58	13.9	11.7	2.21
16	**2d** (0.1)	30	70	0.25	5.0	133[d]	11.80
17[e]	**I** (0.5)	5	25	0.93	22.3	138	2.70
18[e]	**I** (0.5)	5	50	0.88	21.1	57.2	3.84
19[e]	**I** (0.5)	5	70	0.53	12.7	38.3[d]	12.04
20	**I** (0.1)	30	70	0.32	6.4	264[d]	20.74

[a] Conditions: toluene 50 mL, ethylene 1 bar, cocatalyst Et_2AlCl 2.0 mmol, ETA/V = 300 (molar ratio).

[b] Activity in kg of polymer/(mmol$_V$ h).

[c] GPC data in 1,2,4-trichlorobenzene versus polystyrene standards.

[d] Bimodal polymer.

[e] Cited from ref. 23.

2a–d decreased sharply with the increase of polymerization temperature, the molecular weight distribution only slightly changed in the first 5-min polymerization. The observed results were an interesting contrast to those obtained with complex **I**, in which the increase of polymerization temperature resulted in the reduction of activities and broadening molecular weight distributions.

A maximum in activity is also observed with varying Et_2AlCl concentration. As shown in Figure 2, the increase of the ratio of Al/V leads to a steady enhancement of activity first and reaches a maximal value of 13.94 kg/mmol$_V$ h bar when the Al/V equals 4000, and then decreases gradually, whereas the molecular weight of the resultant PEs decreases almost linearly first, then tardily with about Al/V = 4000 as the turning point, indicating chain transferred reaction to Al occurring. In addition, the molecular weight distribution of the resultant polymers also decreases with the increase of Et_2AlCl concentration (PDI = 3.79, Al/V = 500; PDI = 2.19, Al/V = 6000). Other organoaluminum compounds, such as modified MAO, dry MAO, $AlMe_3$, and $AlEt_3$, were also tested as cocatalyst in combination with complex **2c**. However, only **2c**/(modified MAO) system displayed low activity (0.07 kg PE/mmol$_V$ h bar), and trace or even no polymer was obtained using dry MAO, $AlMe_3$, or $AlEt_3$ as the cocatalyst. End-group analysis of the polymer (M_n = 5 600, PDI = 2.34, entry 11 in Table 1) by ^1H and ^{13}C NMR spectroscopy in 1,2-$C_6D_4Cl_2$ found that the chain was terminated

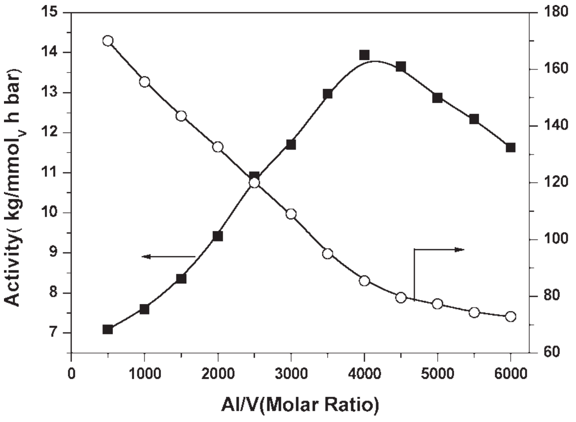


Figure 2. Plots of the activity of catalyst **2c**/Et_2AlCl and the molecular weight of the resultant polymers versus Al/V molar ratio (**2c** 0.5 μmol, V_{total} = 50 mL, ETA/V = 300 mol/mol, 25 °C, polymerization for 5 min).

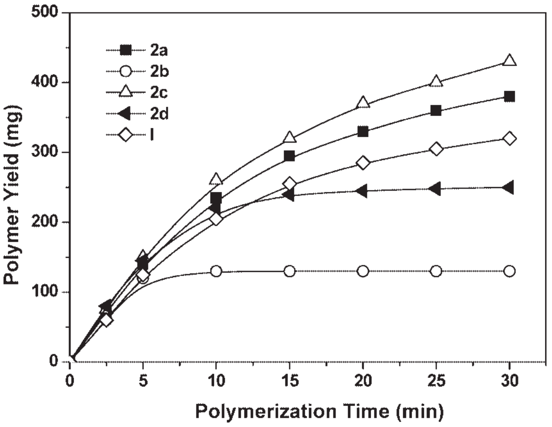


Figure 3. Plots of the productivity of catalysts **2a–d** and **I** versus polymerization time. (Conditions: 1 bar ethylene, catalysts 0.1 μmol, $V_{\mathrm{total}} = 50$ mL, DEAC 0.4 mmol, ETA 0.03 mmol, 70 °C).

by saturated group. These results suggest that chain transfer to aluminum is the main chain transfer reaction. $Cl_3CCOOEt$ has been used as a reactivating agent to reactivate the low-valent, less active, or inactive species to active vanadium (III) species. Similar to the results reported by other groups,[3,4(b),18(a,b)] the activities of **2a–d** in the absence of $Cl_3CCOOEt$ (1.0–4.2 kg PE/mmol$_V$ h bar) are lower than those of in the presence of $Cl_3CCOOEt$ (13.9–18.2 kg PE/mmol$_V$ h bar)) at 70 °C for 5 min.

Catalyst lifetime studies were carried out with catalysts **2a–d** as well as the known catalyst **I** at 70 °C. Catalysts **2b** and **2d** showed little or no ethylene uptake after the first ~10 min, whereas other three catalysts **2a**, **2c**, and **I** maintained some productivity over the full 30-min run time, with the benzothiazole group contained catalyst **2c** being superior (Fig. 3). The PEs obtained with **2a–d** and **I** at 70 °C in 30 min have bimodal molecular weight distribution (Fig. 4). The observed bimodal distribution is probably because of the presence of two types of catalytic active species, the relative distribution of which is dependent on the catalysts utilized.[5(b),8(b),16(g),21(a)] The more dominant high M_w part (~62 and 72 wt % of the total) PEs were formed with **2a** and **2c**, whereas the low M_w fraction (>90 wt % of the total) predominant PEs were obtained by **2b** and **2d** mainly because of the deactivation of catalyst after about 10 min. As shown the GPC curves of the polymers produced by **2c** in Figure 5, compared with the behavior of polymer obtained with 5-min polymerization, which displayed unimodal molecular weight distribution ($M_w = 13{,}300$, $M_w/M_n = 2.34$), the polymer obtained with 15- and 30-min polymerization exhibited bimodal molecular weight distribution. In addition, the $M_{pk1} = 13{,}000$ and 13,700 of the low-molecular-weight fractions in the polymers obtained with 15- and 30-min polymerization, respectively, are close to that of the polymer produced in 5 min ($M_{pk} = 11{,}700$). This result suggests that some species might be reduced to low-valent, less active, or inactive species when polymerization operated at an elevated temperature. Because we do not know the exact active species up to now, we could not completely exclude the possibility of the leaching of the ligand from the coordination sphere of the

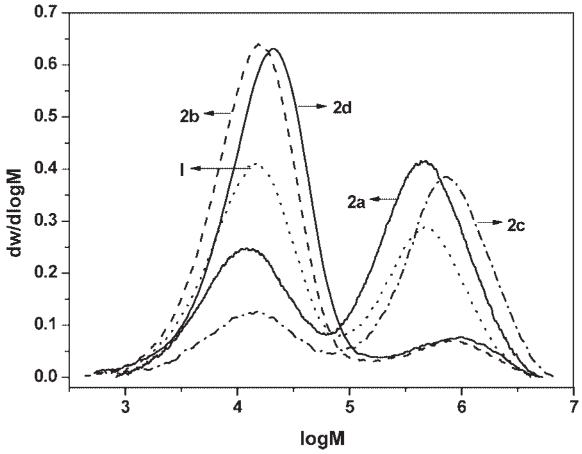


Figure 4. Molecular weight distributions determined by GPC for the PEs produced by catalysts **2a–d** and **I**. (Conditions: 1 bar ethylene, catalysts 0.1 μmol, $V_{\mathrm{total}} = 50$ mL, DEAC 0.4 mmol, ETA 0.03 mmol, 70 °C, polymerization for 30 min).

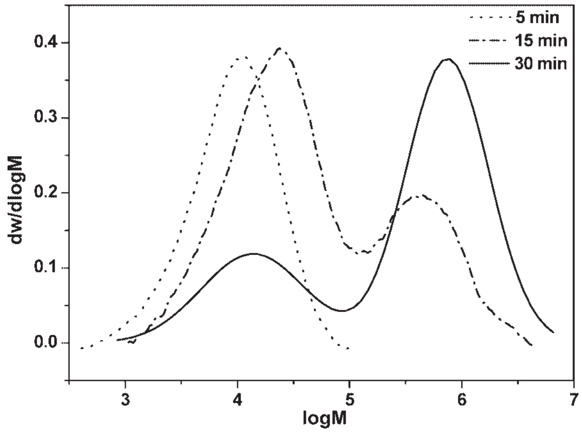


Figure 5. Molecular weight distributions determined by GPC for the PEs produced by catalysts **2c**. (Conditions: 1 bar ethylene, catalyst **2c** 0.1 μmol, $V_{\mathrm{total}} = 50$ mL, DEAC 0.4 mmol, ETA 0.03 mmol, polymerization at 70 °C).

Table 2. Copolymerization of Ethylene and 1-Hexene (Hex) by **2a–d**[a]

Entry	Catalyst	T (min)	T (°C)	Comonomer (mol/L)	Polymer (g)	Activity[b]	Hexene Content[c]	M_{w}[d] ($\times 10^3$)	$M_{\mathrm{w}}/M_{\mathrm{n}}$[d]	T_{m}[e] (°C)
1	2a	10	25	0.27	0.60	3.60	3.05	50.9	2.45	106.9
2	2b	10	25	0.27	0.53	3.18	3.71	58.8	2.41	105.9
3	2c	10	25	0.27	0.65	3.90	2.69	37.1	2.32	109.3
4	2c	10	50	0.27	1.03	6.18	5.20	11.9	2.20	104.6
5	2c	10	70	0.27	0.38	2.28		3.70	1.99	93.3
6	2c	30	25	0.27	1.64	3.28		43.5	2.34	103.3
7	2c	30	50	0.27	1.25	2.50		16.3	2.37	98.6
8	2c	30	70	0.27	0.83	1.66		10.2	2.39	95.6
9	2c	10	50	0.13	1.04	6.84	3.52	15.3	2.05	108.3
10	2c	10	50	0.81	0.62	3.72	10.7	8.62	2.02	80.1
11	2c	10	50	2.70	0.20[f]	1.20	26.7			
12	2d	10	25	0.27	0.27	1.62	3.24	57.0	2.64	106.3

[a] Conditions: toluene + comonomer = 30 mL, catalyst 1.0 μmol, ethylene 1 bar, catalyst 1.0 μmol, cocatalyst Et_2AlCl 4.0 mmol, ETA/V = 300 (molar ratio).

[b] Activity in kg of polymer/(mmol$_V$ h bar).

[c] Comonomer content (mol %) estimated by ^{13}C NMR spectra.

[d] GPC data in 1,2,4-trichlorobenzene versus polystyrene standard.

[e] Determined by DSC.

[f] Obtained as waxy polymer.

vanadium when polymerization was operated at 70 °C in 30 min. Similar results were observed by other groups. For example, bimodal molecular weight distribution polymer was produced by trivalent vanadium diimine/pyridine complex, though the diimine/pyridine ligand is strongly bound to vanadium when vanadium complex was exposed to alkylaluminum cocatalysts.[8(b)] Wide molecular weight distribution polymer was also obtained by tetravalent vanadium salphen complexes.[21(a)] An alternative explanation involves coordinative chain-transfer polymerization[31] in which rapid chain transfer to aluminum compounds exists. However, in the current catalyst system, chain transfer to aluminum is not fast enough to meet the requirements of coordinative chain-transfer polymerization, leading to bimodal molecular weight distribution of PE.

Ethylene/Hexene Copolymerizations

The representative results of ethylene/1-hexene copolymerization catalyzed by **2a–d** are summarized in Table 2. All the catalysts show high activities toward copolymerization and produce the high-molecular-weight copolymers with unimodal molecular weight distributions. Under the same conditions, catalyst **2c** exhibits the highest catalytic activity (3.90 kg/mmol$_V$ h), followed by **2a** (3.60 kg/mmol$_V$ h), **2b** (3.18 kg/mmol$_V$ h), and **2d** (1.62 kg/mmol$_V$ h). The data of entries 1–3 and 12 in Table 2 indicate that the abilities of these vanadium catalysts to copolymerize ethylene and 1-hexene are similar. No obvious difference in 1-hexene incorporations (from 2.69 to 3.71 mol %) was observed.

The effect of reaction conditions on the copolymerization of ethylene/1-hexene was also investigated using catalyst **2c**. With the increase of 1-hexene in feed, the catalytic activity toward the copolymerizations decreases gradually, and the molecular weight of the resultant copolymers also declines, whereas 1-hexene incorporation gradually increases up to 26.7 mol % when 1-hexene concentration was 2.70 mol/L. The data of entries 3–8 in Table 2 indicate that catalytic activity and the molecular weight of resultant copolymers also depend on reaction temperature and polymerization time. The highest catalytic activity (6.18 kg/mmol$_V$ h) was achieved at 50 °C for **2c** when polymerization runs for 10 min. However, when polymerization time extended to 30 min, the most productive temperature was 25 °C, which showed comparable activity with that in 10 min. The molecular weight of the resultant copolymers decreased sharply with the increase of polymerization temperature (Fig. 6). Noted that molecular weight distribution of the resultant polymer is independent of polymerization temperature, even at 70 °C polymerization for 30 min, unimodal molecular weight distribution copolymer was produced, indicating a single-site catalytic behavior. Furthermore, prolonging polymerization time is

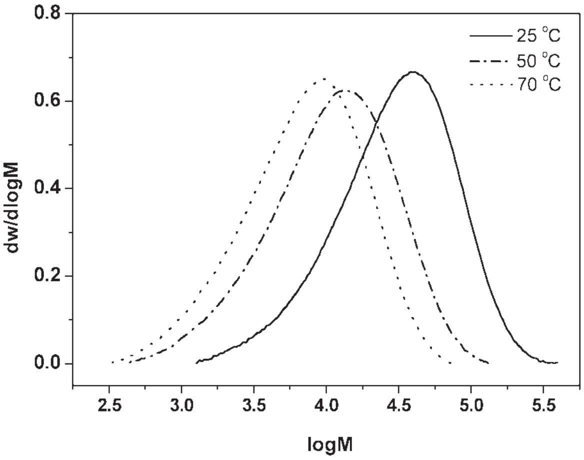
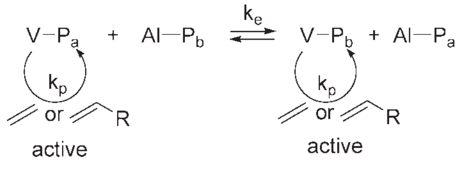


Figure 6. Molecular weight distributions determined by GPC for the ethylene and 1-hexene copolymers produced by catalysts **2c**. (Conditions: 1 bar ethylene, catalyst **2c** 1.0 μmol, $V_{\mathrm{total}} = 30$ mL, 1-hexene 8.1 mmol, DEAC 4 mmol, ETA 0.3 mmol, polymerization for 30 min).

beneficial to increase the molecular weight of resultant copolymers with slightly broadening molecular weight distributions (e.g., Table 2 entry 5 vs. entry 8). In addition, the 1-hexene incorporation also increased with elevating polymerization temperature (entries 3 and 4 in Table 2).

The differences in behavior between ethylene polymerization and ethylene/hexene copolymerization, with regard to catalytic activity, molecular weight, and molecular weight distribution of the resultant polymers, could rise from a variety of reasons. For example, the introduction of bulkier comonomer may decrease the rate of olefin insertion into the vanadium carbon bond (k_p) (see Scheme 3), but the rate of exchange of the polymer chains between vanadium and Al (k_e) must be kept constant, so the ratio of k_e/k_p in ethylene and 1-hexene copolymerization could be much higher than that in homopolymerization, though it may be not high enough to the criterion of catalyzed chain growth ($k_e \gg k_p$).[31(f)] Hence, catalytic activity, molecular weight, and molecular weight distribution of the resultant polymers decreased in copolymerization.



Scheme 3. Generic mechanism for catalyzed chain growth.

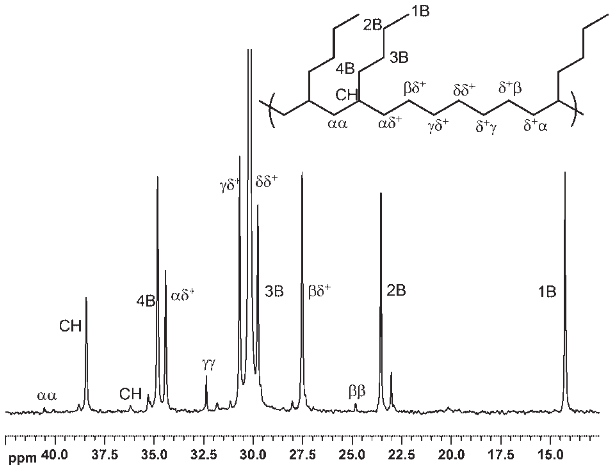


Figure 7. ^{13}C NMR spectra of the ethylene/1-hexene copolymers obtained with catalyst **2c**/Et$_2$AlCl (entry 10, Table 2).

The microstructures of the ethylene/1-hexene copolymers have been analyzed using ^{13}C NMR techniques. The percentage of comonomer incorporation in the copolymer chain was calculated with the literature reported method.[32] Figure 7 shows the typical ^{13}C NMR spectra of ethylene/1-hexene copolymers (more figures of ^{13}C NMR were listed in Supporting Information). The 1-hexene units are usually isolated between the ethylene units, but the block-type sequence of 1-hexene appeared when more comononer incorporated. Triad distribution data arising from ^{13}C NMR analysis of poly(ethylene-*co*-hexene)s produced by **2c** were summarized in Table S1 (see Supporting information). We found that HEH triads appeared (0.4 mol %) in poly(ethylene-*co*-hexene) with 10.7 mol % hexene incorporation, and EHH sequence also increased (from 4.3 to 7.1 mol %) when compared with that of 5.2 mol % hexene incorporation. Moreover, HHH triads were observed (0.1 mol %) in the copolymer with 26.7 mol % hexene incorporation. This behavior is similar to the copolymer obtained by tridentate Schiff Base-chelated vanadium catalysts.[26(b)] However, it is different from those produced by the mono(β-enaminoketonato) vanadium(III) catalysts, which contained only isolated hexene units even with high 1-hexene incorporation (16.0 mol %).[20]

CONCLUSIONS

In this work, we reported a series of novel vanadium(III) complexes bearing salicylaldiminato ligands as catalysts for olefin polymerization. In the presence of Et$_2$AlCl, heteroatom-containing

Schiff Base ligands-chelated vanadium(III) complexes showed high activities toward ethylene polymerization and produced high-molecular-weight polymers at an elevated temperature. Both catalyst structure and reaction temperature considerably influence catalytic activity, molecular weight, and molecular weight distribution, especially distribution modal, of the resultant polymers. The activities observed for the benzothiazole-containing vanadium(III) complex were excellent at 70 °C. The cocatalyst concentration was found to significantly affect the polymerization activity and chain transfer events. These catalysts also displayed remarkable activity toward ethylene/hexene copolymerization. High molecular weight with unimodal molecular weight distribution copolymers were obtained even at an elevated polymerization temperature. Although in some cases the observed catalytic behavior could be explained by catalyst structure and reaction conditions, there are still features that are not well clarified. Further investigation of related systems should lead to a better understanding of the important characteristics of these catalysts for controlling the molecular weight and molecular weight distribution of the polymers.

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