

ETHYLENE/1-HEXENE COPOLYMERIZATION BY SALICYLALDIMINATO VANADIUM(III) COMPLEXES ACTIVATED WITH DIETHYLALUMINUM CHLORIDE*

Ji-qian Wu, Yan-guo Li, Bai-xiang Li and Yue-sheng Li**

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China

Abstract Mono salicylaldiminato vanadium(III) complexes (**1a–1f**) [$\text{RN} = \text{CH}(\text{ArO})\text{VCl}_2(\text{THF})_2$ ($\text{Ar} = \text{C}_6\text{H}_4$ (**1a–1e**), $\text{R} = \text{Ph}$, **1a**; $\text{R} = p\text{-CF}_3\text{Ph}$, **1b**; $\text{R} = 2,6\text{-Me}_2\text{Ph}$, **1c**; $\text{R} = 2,6\text{-iPr}_2\text{Ph}$, **1d**; $\text{R} = \text{cyclohexyl}$, **1e**; $\text{Ar} = \text{C}_6\text{H}_2\text{tBu}_2(2,4)$, $\text{R} = 2,6\text{-iPr}_2\text{Ph}$, **1f**) and bis(salicylaldiminato) vanadium(III) complexes (**2a–2f**) [$\text{RN} = \text{CH}(\text{ArO})_2\text{VCl}(\text{THF})_x$ ($\text{Ar} = \text{C}_6\text{H}_4$ (**2a–2e**), $x = 1$ (**2a–2e**), $\text{R} = \text{Ph}$, **2a**; $\text{R} = p\text{-CF}_3\text{Ph}$, **2b**; $\text{R} = 2,6\text{-Me}_2\text{Ph}$, **2c**; $\text{R} = 2,6\text{-iPr}_2\text{Ph}$, **2d**; $\text{R} = \text{cyclohexyl}$, **2e**; $\text{Ar} = \text{C}_6\text{H}_2\text{tBu}_2(2,4)$, $\text{R} = 2,6\text{-iPr}_2\text{Ph}$, $x = 0$, **2f**) have been evaluated as the active catalysts for ethylene/1-hexene copolymerization in the presence of Et_2AlCl . The ligand substitution pattern and the catalyst structure model significantly influenced the polymerization behaviors such as the catalytic activity, the molecular weight and molecular weight distribution of the copolymers *etc.* The highest catalytic activity of 8.82 kg PE/(mmol $\cdot$ h) was observed for vanadium catalyst **2d** with two 2,6-diisopropylphenyl substituted salicylaldiminato ligands. The copolymer with the highest molecular weight was obtained by using mono salicylaldiminato vanadium catalyst **1f** having ligands with *tert*-butyl at the *ortho* and *para* of the aryloxy moiety.

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

INTRODUCTION

Polyethylene is the largest volume polymer consumed in the world. It is a versatile polymer that offers high performance relative to other polymers and alternative materials such as glass, metal or paper. The density of polyethylene, one of the critical parameters influencing its properties, is controlled by the level and distribution of branching. The copolymerization of ethylene with α -olefin introduces short-chain branching into the chain backbone, resulting in the linear low-density polyethylene (LLDPE). Polymer properties, such as melting and glass transition temperatures, melt viscosity, and mechanical or optical properties are largely dependent on the incorporation and distribution of α -olefins. Controlled amounts of α -olefins in polyethylene with uniform and homogeneous sequence and composition distributions can be achieved by new generations of catalysts. Among the many transition metals that produce interesting catalysts for olefin polymerization, without doubt, vanadium occupies a special position. Since the 1950s, vanadium catalysts have played a critically important role in producing polyethylenes of high molecular weight with narrow molecular weight distribution as well as α -olefin or cycloolefin copolymers with high comonomer incorporations^[1–4]. The vanadium-based Ziegler/Natta technology is still among the most widely used catalytic systems for the worldwide commercial production of synthetic rubber and elastomers (EPDM). However, the activity of vanadium catalyst is often much lower than that displayed by Group IV based catalysts^[5–11]. Despite there has been considerable researches concerning this

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** Corresponding author: Yue-sheng Li (李悦生), E-mail: ysl@ciac.jl.cn

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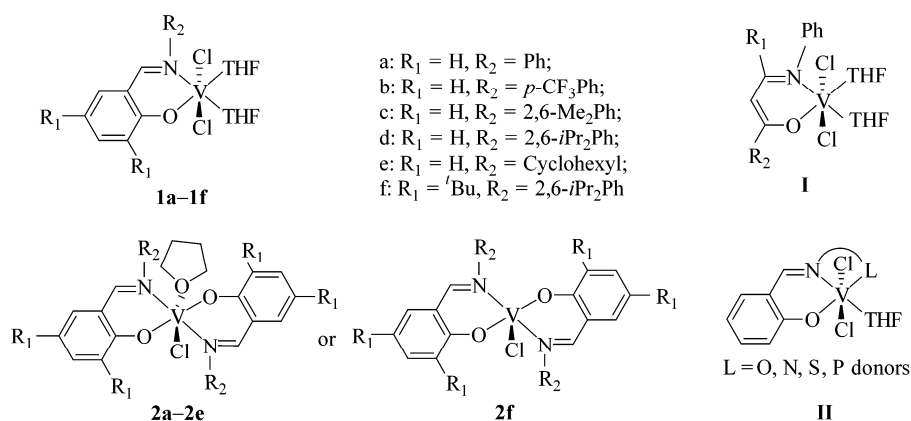
issue^[12–21], our understanding of the relationship between the catalyst structure and its ability to incorporate monomers is incomplete.

Previously, we found that the vanadium(III) complexes bearing bidentate salicylaldiminato ligands were efficient catalysts for ethylene polymerization^[15]. Subsequently researches showed that Schiff base ligands containing pendant heteroatoms such as O, N, S, P can also be used to stabilize vanadium(III) catalysts which displayed high catalytic activities at high polymerization temperatures for ethylene polymerization and promising capability towards copolymerization of ethylene with 1-hexene or nobornene^[16]. Pendant groups in the tridentate ligands chelate vanadium catalysts are supposed to partly encumber the insertion of comonomers^[17], so we like to extend our interest to investigate the effect of ligand substitution pattern and catalyst structure model on ethylene/1-hexene copolymerization behaviors of bidentate salicylaldiminato vanadium(III) complexes.

EXPERIMENTAL

General Procedures and Materials

The manipulation of air- and/or moisture-sensitive compounds was carried out entirely under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of polymers were obtained on a Varian Unity-400 MHz spectrometer at 135°C, respectively, with *o*-C₆D₄Cl₂ as a solvent. The 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 μ m 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 standards EasiCal PS-1 (PL Ltd). Ethyl trichloroacetate (ETA) was purchased from Aldrich, dried over calcium hydride at room temperature and then distilled. Diethylaluminium chloride (DEAC) was obtained from Albemarle Corporation. Literature procedures were used to synthesize complexes **1a–1f**^[15], **2a–2f**^[15], **I**^[14] and **II** (Scheme 1)^[17].



Scheme 1 Salicylaldiminato and β -enaminoketonato vanadium(III) catalysts

General Procedure for Ethylene (Co)Polymerization

Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Toluene, Et₂AlCl, ETA and comonomer were charged into the autoclave in sequence in the drybox. The autoclave was placed under ethylene atmosphere (0.101 MPa). After the addition of a toluene solution containing a prescribed amount of catalyst *via* a syringe, the reactor was sealed and pressurized to the desired level, and the stirring motor was engaged. After the prescribed reaction time, the stirring motor was stopped and the reactor was vented, and the resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol and dried at 60°C for 12 h *in vacuo*.

RESULTS AND DISCUSSION

Ethylene/1-Hexene Copolymerization by Mono Salicylaldiminato Vanadium(III) Catalysts

As the salicylaldiminato ligand has multiple sites for introducing or changing the substituents, the steric and electronic requirements of the metal center can be modulated easily by varying the ligand structure. By variation of the substituents (R_1 and R_2), we obtained a series of highly efficient catalysts toward ethylene polymerization. Further investigation showed that positive results were available by bis(salicylaldiminato) vanadium complexes at high polymerization temperature. To investigate the effect of ligand structure on the catalytic activity and properties of the resultant polymer, we selected a series of vanadium complexes bearing one or two bidentate salicylaldiminato ligands as our object. In addition, β -enaminoketonato and tridentate salicylaldiminato vanadium complexes were also selected for comparison.

The effect of reaction conditions on the copolymerization of ethylene/1-hexene was investigated using catalyst **1a**. The typical results are summarized Table 1. The data in Table 1 (entries 1–5) indicate that both the catalytic activity and the molecular weight (M_w) of the copolymers are remarkably influenced by Et_2AlCl concentration. The increase of the ratio of Al/V leads to a steady enhancement of activity while a gradual decrease of M_w indicates the occurring of chain transfer reaction to Al. This result was similar to the ethylene polymerization by **1a**, but they were quite different from the previously reported β -enaminoketonato catalytic systems, in which M_w was independent of Et_2AlCl concentration^[14]. Interestingly, the molecular weight distribution was unimodal (PDI = 2.10–2.35) and slightly dependent on the Al/V molar ratio, this result was different from the ethylene homopolymerization which showed broad molecular weight distribution at low cocatalyst concentration but displayed unimodal molecular weight distribution when Al/V equaled 6000^[15–17]. The 1-hexene incorporation was slightly changed when the ratio of Al/V increased from 500 to 6000.

Table 1. Effect of reaction temperature and cocatalyst concentration on ethylene/hexene copolymerizations by **1a** and **2a**^a

Entry	Catalyst	T (°C)	Al/V ^b (mol/mol)	Polymer (g)	Activity ^c	1-Hexene content ^d	$M_w^e \times 10^{-3}$	M_w/M_n^e	T_m^f (°C)
1	1a	25	500	0.43	2.58	3.45	62.1	2.35	105.2
2	1a	25	1000	0.88	5.28	3.56	47.5	2.27	104.9
3	1a	25	2000	1.09	6.54	3.50	39.7	2.10	105.2
4	1a	25	4000	1.26	7.56	3.50	34.5	2.16	105.4
5	1a	25	6000	1.34	8.02	3.68	25.2	2.12	101.1
6	1a	50	4000	0.65	3.90	8.02	9.1	2.84	96.8
7	1a	70	4000	0.28	1.68	9.87	4.0	2.10	97.1
8	2a	25	4000	0.53	3.18	3.26	36.1	2.21	106.8
9	2a	50	4000	0.45	2.70	7.19	36.5	2.16	99.3
10	2a	70	4000	0.39	2.34	9.69	8.6	2.48	96.4

^a Conditions: toluene + comonomer = 30 mL, ethylene 0.101 MPa, 1-hexene 1.0 mL, catalyst 1.0 μmol , $\text{ETA/V} = 300$ (molar ratio), copolymerization for 10 min; ^b Cocatalyst Et_2AlCl ; ^c Activity in kg of polymer/(mmol $\cdot$ h); ^d Comonomer content (mol%) estimated by ^{13}C -NMR spectra; ^e GPC data in *o*-dichlorobenzene versus polystyrene standards; ^f Determined by DSC

The data of entries 4, 6 and 7 in Table 1 indicate that catalytic activity and the molecular weight of resultant copolymers largely depend on reaction temperature. A sharp decrease of activity and molecular weight was observed when polymerization temperature was elevated from 25°C to 75°C. However, the molecular weight distributions of copolymers were unimodal and independent of reaction temperature, indicating the single site catalyzing behavior. Much more 1-hexene was incorporated at 75°C than at 25°C. This result may arise from a variety of reasons, for example, the ethylene concentration was lower at the higher reaction temperature, the barrier of hexene insertion reaction was much higher than that of ethylene *etc.* Redshaw and his coworkers have also observed the dependence of activity and molecular weight on polymerization temperature when $\text{N}_2\text{O}_2\text{S}_2$ -based ligands chelated vanadium catalysts were applied to catalyze ethylene/1-hexene polymerization^[22].

With the increase of 1-hexene in feed, the catalytic activity towards the copolymerizations decreases

gradually, while 1-hexene incorporation almost linearly increases up to 12.2 mol% when 1-hexene concentration is 1.07 mol/L (Fig. 1). As shown in Fig. 2, the molecular weight of the resultant copolymers also declines when much more comonomer is charged, but slight changes of molecular weight distribution are observed. The melting temperature and the degree of crystallinity of the copolymer were also significantly influenced by the initial 1-hexene concentration (Fig. 3), both decreased with the increase of 1-hexene incorporation. The microstructures of the ethylene/1-hexene copolymers have been analyzed *via* NMR spectra. The comonomer incorporation in the copolymer chain was calculated with the method of Randall and coworkers^[22]. As shown in Fig. 4, the 1-hexene units are usually isolated between the ethylene units, but when the comonomer incorporation increased up to 12.2 mol% the block type sequence of hexene appeared (the peak assigned as $\alpha\alpha$). The behavior is consistent with the copolymers produced by previous reported tridentate salicylaldiminato vanadium(III) catalysts^[17], however, it is different from the resultant polymers obtained by the corresponding mono(β -enaminoketonato) vanadium(III) catalysts or $\text{VCl}_3(\text{THF})_3$ which only contain isolated 1-hexene units even with high 1-hexene incorporation (16.0%)^[14].

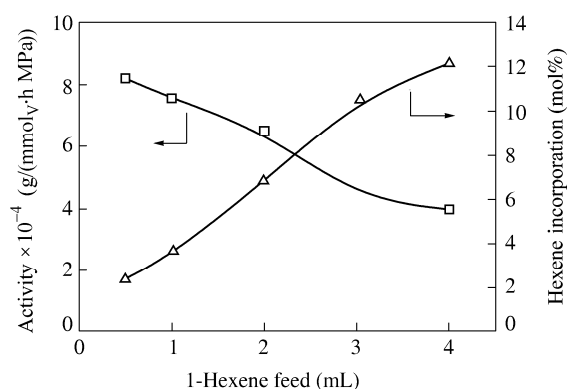


Fig. 1 Plots of the activity of **1a**/ Et_2AlCl and the 1-hexene incorporation versus comonomer content in the feed

1a 1 μmol , Et_2AlCl 4 mmol, ETA 0.3 mmol, V_{total} = 30 mL, 25°C, polymerization for 10 min

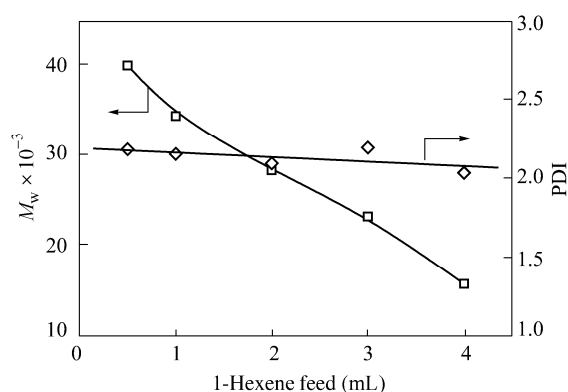


Fig. 2 Plots of molecular weight and molecular weight distribution of the copolymers produced with **1a**/ Et_2AlCl versus comonomer content in the feed

1a 1 μmol , Et_2AlCl 4 mmol, ETA 0.3 mmol, V_{total} = 30 mL, 25°C, polymerization for 10 min

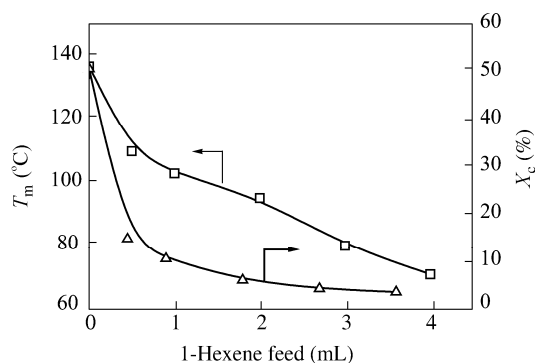


Fig. 3 Plots of the melting temperature and degree of crystallinity of polymers obtained by **1a**/ Et_2AlCl versus 1-hexene in the feed

1a 1 μmol , Et_2AlCl 4 mmol, ETA 0.3 mmol, V_{total} = 30 mL, 25°C, polymerization for 10 min

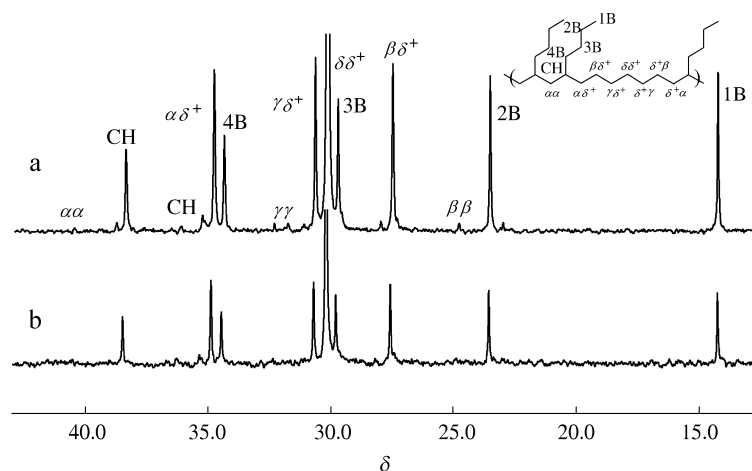


Fig. 4 ^{13}C -NMR spectra of the ethylene/1-hexene copolymers obtained with catalyst **1a**/ Et_2AlCl : 1-hexene incorporation (a) 12.2 mol%, (b) 9.87 mol%

Table 2. Copolymerization of ethylene and 1-hexene by **1a–1f**, **2a–2f**^a

Entry	Catalyst	Polymer (g)	Activity ^b	1-Hexene content ^c	$M_w^d \times 10^{-3}$	M_w/M_n^d	T_m^e (°C)
1	1a	1.26	7.56	3.50	34.5	2.16	105.4
2	1b	1.14	6.84	3.54	45.8	1.86	109.8
3	1c	1.11	6.66	3.58	33.0	2.46	105.8
4	1d	1.09	6.54	3.58	33.0	2.46	105.8
5	1e	1.00	6.00	4.01	31.9	2.06	104.8
6	1f	0.95	5.70	3.69	60.1	2.28	106.1
7	2a	0.53	3.18	3.26	36.1	2.21	106.8
8	2b	1.30	7.80	4.57	4.80	2.30	104.3
9	2c	0.87	5.22	3.15	32.3	2.19	107.4
10	2d	1.47	8.82	3.09	28.0	2.24	108.2
11	2e	0.15	0.90	2.75	37.2	2.01	109.5
12	2f	trace					
13	I ^f	0.23	1.38	5.40	148	2.20	103.5
14	II ^g	0.53	3.18	3.00	56.4	2.00	108.0

^a Conditions: toluene + comonomer = 30 mL, ethylene 0.101 MPa, 1-hexene 1.0 mL, catalyst 1.0 μmol , ETA/V = 300 (molar ratio), Et_2AlCl 4 mmol, 25°C, 10 min; ^b Activity in kg of polymer/(mmol $\cdot$ h); ^c Comonomer content (mol%) estimated by ^{13}C -NMR spectra; ^d GPC data in *o*-dichlorobenzene versus polystyrene standards; ^e Determined by DSC; ^f $[\text{PhN} = \text{CHCHC}(\text{Ph})\text{O}]\text{VCl}_2(\text{THF})_2$; ^g $[\text{OC}_6\text{H}_4\text{CH} = \text{NCH}_2\text{C}_5\text{H}_4\text{N}]\text{VCl}_2(\text{THF})$, data cited from Ref. [17]

The representative results of ethylene/1-hexene copolymerization catalyzed by **1a–1f** are summarized in Table 2. All of the catalysts show high activities toward the copolymerization, and produce the copolymers with high molecular weight and unimodal molecular weight distributions. Among the six catalytic systems, catalyst **1a** without substituent on the salicylaldiminato ligand exhibited the highest activity of 7.56 kg polymer/(mmol $\cdot$ h). With the introduction of bulky group on the imino phenyl or the aryloxy moiety of the ligand, the catalytic activities of **1c**, **1d** and **1f** were lower than that of **1a**, and the activity decreased in the order: **1f** < **1d** < **1c** < **1a**, indicating the influence of steric hindrance in the monomer insertion reaction. Neither obvious difference in 1-hexene incorporations nor enhancement of molecular weight of the copolymers was observed when the steric group was introduced into the imino moiety. Interesting, however, among the six mono salicylaldiminato vanadium(III) catalysts, catalyst **1f** bearing ligands with *tert*-butyl at the *ortho* and *para* of the aryloxy moiety produced the copolymer with highest molecular weight, and the comonomer incorporations by different catalysts were comparable. This indicates that the bulky group in the aryloxy moiety could partly

hinder the chain transfer reactions. Catalysts **1a**, **1b** and **1e** with different electronic feature on the imino display a distinction in catalytic activity and molecular weight of the copolymer. Introducing *p*-CF₃ into the N-aryl moiety of the ligand (catalyst **1b**) resulted in a slight decrease of the catalytic activity, but catalyst **1b** was observed to yield the copolymer with higher molecular weight than that of **1a**. The copolymer with highest 1-hexene incorporation and lowest molecular weight was produced by catalyst **1e**, which bore nonconjugate group (cyclohexyl) on the imino.

Results for ethylene/hexene copolymerization by mono β -enaminoketonato vanadium complex (**I**) and tridentate salicylaldiminato vanadium complex (**II**) are also summarized in Table 2. Much lower activities were observed for **I** and **II** than that of mono salicylaldiminato vanadium(III) catalyst **1a** under the same conditions. The molecular weight of the copolymer produced by **I** was more than four times higher than that by using **1a**. It is important to note that higher 1-hexene incorporation copolymer was also observed for **I**. The more open framework of β -enaminoketonato ligand than salicylaldiminato ligand may be responsible for incorporating high amount of comonomer. These results suggested that the ligand framework may directly affect the ethylene/1-hexene copolymerization behaviors.

Ethylene/1-Hexene Copolymerization by Bis(salicylaldiminato) Vanadium(III) Catalysts

The catalytic activities of **2a–2f** for the copolymerizations are also listed in Tables 1 and 2. The catalytic behaviors of catalyst **2a**, especially the properties of the resultant copolymers, were also sensitive to polymerization temperature (see entries 8–10 in Table 1). The catalytic activity gradually decreased when polymerization temperature was elevated from 25°C to 70°C. It is interesting to note that **2a** exhibited higher activity than **1a** when polymerization operated at 70°C, although **2a** only displayed much lower activity than **1a** at 25°C. The unimodal molecular weight distributions for the resultant poly(ethylene-*co*-hexene) (PDI = 2.16–2.48) were observed if **2a** was used as the catalyst in the range of the polymerization temperature tested. It was revealed that the molecular weight of the copolymer obtained at 25°C was almost the same as that produced at 50°C, but a sharp decrease of molecular weight was observed with increasing the temperature to 70°C. It is noteworthy that the copolymers obtained by **2a** displayed higher molecular weight, especially when polymerization was operated at high temperatures, than those by **1a**. The origin of these differences remains obscure, but it appears that the introduction of one more salicylaldiminato ligand is beneficial to stabilizing the catalytic species. In addition, the 1-hexene incorporation also increased upon the elevation of polymerization temperature.

Bis(salicylaldiminato) vanadium catalysts **2a–2e** are all highly active towards ethylene/1-hexene copolymerization in the presence of Et₂AlCl. The 2,6-diisopropylphenyl substituted salicylaldiminato ligand chelating vanadium catalyst (**2d**, 8.82 kg polymer/(mmol $\cdot$ h)) shows the highest activity under the similar conditions. The activities increased in the order: **2a** (3.18) < **2c** (5.22) < **2d** (8.82 kg polymer/(mmol $\cdot$ h)) which can be explained from the structure of catalysts, as we have previously discussed^[15], the increase of steric group on the N-moiety has a direct effect on the configuration of bis(salicylaldiminato) vanadium(III) complexes. The **2d** with Cl and THF in *cis* geometry probably is the most suitable precursor for the ethylene insertion reaction. The molecular weight of copolymers decreased with the increase of the steric hindrance on the imino. This result may be related to the chain transfer to Al, which was enhanced with increased steric hindrance at the active vanadium centre. The lowest activity of **2f** is due to bulky substituents on both the N-moiety and aryloxy moiety of the salicylaldiminato ligand which leave little room for the monomer to coordinate with vanadium, evidenced by the X-ray structure of catalyst **2f**^[15]. These results were consistent with the behavior of ethylene homopolymerization, which was established to be highly dependent upon the steric hindrance of the ligands^[15]. The electronic groups on the ligands can be used to tune the catalytic activities as evidenced by the fact that *p*-CF₃phenyl substituent on the N-moiety increases the catalytic activity (entry 8, 7.80 kg polymer/(mmol $\cdot$ h)) while cyclohexyl group causes a sharp drop in activity (entry 11, 0.90 kg polymer/(mmol $\cdot$ h)). The copolymer with lowest molecular weight and highest 1-hexene incorporation was produced by catalyst **2b** among bis(salicylaldiminato) vanadium catalysts under the same conditions. This may be due to the more positive

vanadium centre which was obtained by the introduction of the strong withdrawing group on the imino, and this specified electronic environment was particularly adept at 1-hexene incorporation.

CONCLUSIONS

All of the salicylaldiminato vanadium(III) catalysts show high activities toward ethylene/1-hexene copolymerization and produce the copolymers with high molecular weight and unimodal molecular weight distributions under optimized conditions. The steric and electronic effects of the substituents of the ligands and catalyst structure model considerably influence the catalytic activity, comonomer incorporation, molecular weight and molecular weight distribution of the copolymers. The activities of bis(salicylaldiminato) vanadium catalysts were highly dependent upon the steric hindrance of the ligands. Vanadium catalyst **2d** with 2,6-diisopropylphenyl on the N-moiety showed the highest activity, however, the lowest activity was observed when the catalyst bore two salicylaldiminato ligands which contain bulky substituents on both the N-moiety and aryloxy moiety. The copolymer with lowest molecular weight and highest 1-hexene incorporation was produced by bis(salicylaldiminato) vanadium(III) catalyst **2b** which contained highly electron withdrawing group on the N-moiety. In addition, the microstructure of the copolymers can be controlled over a wide range by the variation of catalyst structure and the reaction parameters such as Al/V molar ratio, comonomer feed concentration and polymerization temperature.

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