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Copolymerizations of ethylene with α-olefin-ω-ols by highly active vanadium(III) catalysts bearing [N,O] bidentate chelated ligands

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ABSTRACT

The copolymerizations of ethylene with polar hydroxyl monomers such as 10-undecen-1-ol, 5-hexen-1-ol and 3-buten-1-ol were investigated by the vanadium(III) catalysts bearing bidentate [N,O] ligands (**1**, [PhN=C(CH_3)CHC(Ph)O]VCl_2(THF)$_2$; **2**, [PhN=CHC_6H_4O]VCl_2(THF)$_2$; **3**, [PhN=CHC(Ph)CHO]VCl_2(THF)$_2$). The polar monomers were pretreated by alkylaluminum before the polymerization. High catalytic activities and efficient comonomer incorporations can be easily obtained by changing monomer masking reagents and polymerization conditions in the presence of diethylaluminium chloride as a cocatalyst. The longer the spacer group, the higher the incorporation of the monomer. Under the mild conditions, the incorporation level of 10-undecen-1-ol reached 13.9 mol% in the resultant copolymers was obtained. The reactivity ratios of copolymerization ($r_1 = 41.4$, $r_2 = 0.02$, $r_1r_2 = 0.83$) were evaluated by Fineman–Ross method. According to ^{13}C NMR spectra, polar units were located both on the main chain and at the chain end. The end-hydroxylated polymers were probably obtained due to the formation of dormant species after the insertion of the comonomer followed by the chain transfer to alkylaluminum. In addition, the signals derived from polar monomer inverse insertion were detected for the first time.

1. Introduction

The incorporation of polar groups in polyolefin chains not only can provide the polymers with improved properties, but also offers the sites for initiating graft copolymerization [1–10]. Direct copolymerizing olefin with polar monomer in which functional group closes to vinyl bond by traditional Ziegler–Natta or metallocene catalysts is restricted since the nonbonded electron pairs of heteroatoms tend to form complexes with the metal center. Thus, a preferred current approach to the synthesis of functional polyolefins is the use of monomers possessing long methylene spacers between polar and vinyl groups like in the case of 5-hexen-1-ol, 10-undecen-1-ol and 10-undecenoic acid etc. [11–32]. A number of metallocene catalysts were efficiently tested to produce ethylene/polar monomers copolymers. For example, Seppala, Lofgren and their coworkers explored ethylene/10-undecen-1-ol copolymerizations using a series of metallocene catalysts in the presence of excess methylaluminoxane (MAO) as the cocatalyst and monomer masking reagent [11–13]. Fink and his coworkers utilized $Me_2Si(Ind)_2ZrCl_2$/MAO system to promote the copolymerizations of ethylene with 10-undecene-1-oxytrimethylsilane or 10-undecene-1-oxytriisopropylsilane, in which high catalytic activities and comonomer incorporations were obtained with the triisopropylsilyl protected monomers [14]. Imuta established the end-site-selective introduction of an alcohol group into polyolefins by the combination of metallocene “IF catalyst” with alkylaluminums as a monomer masking reagent, which provided the strategic basis for controlling the regioselectivity in the one-pot synthesis of hydroxyl-capped polyolefins [17]. Shiono and his colleagues reported the copolymerization of ethylene or propylene with 5-hexen-1-ol by $Me_2Si(Flu)_2ZrCl_2$, and alternating poly(ethylene-*co*-5- hexen-1-ol)s were easily obtained under the mild conditions [20].

Compared with group IV metals, vanadium compounds or metal exhibits the reduced oxophilicity. Therefore, the enhanced functional group tolerance makes them much attractive for the incorporation of polar monomers into polyolefin backbone. In recent years, a number of well-defined vanadium catalysts have been used in ethylene polymerization or copolymerization with α-olefins [34–48]. However, successful examples concerning the controlled copolymerization of ethylene with polar monomers by vanadium catalysts are limited so far. Our interest is to explore ethylene/polar monomers copolymerizations with vanadium catalysts, further to prepare polyolefins bearing functional groups in the side chain. The 10-Undecen-1-ol, 5-hexen-1-ol and 3-buten-1-ol with different

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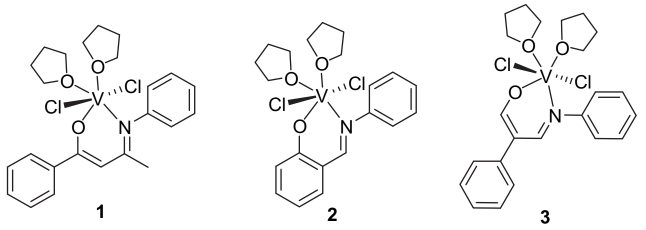


Scheme 1. Vanadium(III) complexes **1**–**3**.

spacer lengths between the functional group and the polymerizable double bond are selected as the polar comonomers to incorporate functional groups into polyolefin chains. In this contributor, we thus explored the copolymerization of ethylene with these functional α-olefins using the vanadium(III) catalysts bearing [N,O] ligands (Scheme 1). These catalysts exhibited remarkable activities and copolymerization abilities in the presence of alkylaluminums as the monomer masking reagents, yielding the copolymers with high functional comonomer incorporation.

2. Experimental

2.1. General

All manipulation of air- and/or moisture-sensitive compounds was carried out 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. Commercial ethylene was directly used for polymerization without further purification. The polar comonomers such as 10-Undecen-1-ol, 5-hexen-1-ol and 3-butylene-1-ol, and ethyl trichloroacetate (ETA) were purchased from Aldrich, dried over calcium hydride at room temperature and then distilled. Diethylaluminium chloride (DEAC), triisobutylaluminum (TiBA), triethylaluminum (TEA) and trimethylaluminum (TMA) were purchased from Albemarle Corporation. The vanadium complexes **1**–**3** were synthesized according to the procedures reported previously [33,34].

2.2. Characterization of the polymers

The ^{1}H and ^{13}C NMR data of copolymers were obtained on a Varian Unity-400 MHz spectrometer at 110 °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 (MW) and the molecular weight distribution (MWD) 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).

2.3. Ethylene/polar monomer copolymerization

The copolymerization was carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. The reactor was charged with 30 mL of toluene and the prescribed amount of polar monomer (10-undecen-1-ol, 5-hexen-1-ol, or 3-butylene-1-ol) and an equivalent amounts of protection reagent (DEAC, TMA, TEA or TiBA), then the ethylene gas feed was started followed by equilibration at desired polymerization temperature. After 10 min, a solution of DEAC in toluene and a solution of ETA in toluene were added. Subsequently, a toluene solution of catalyst was added into the reactor with vigorous stirring (900 rpm) to initiate polymerization. The total volume of the liquid phase was 50 mL. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction. The resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol and acetone, and dried at 60 °C for 24 h in a vacuum oven.

2.4. Ethylene/hexene copolymerization

The 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 30 mL of toluene and the prescribed amount of 1-hexene, and then the ethylene gas feed was started followed by equilibration at desired polymerization temperature. After 10 min, a solution of DEAC in toluene and a solution of ETA in toluene were added. Subsequently, a toluene solution of catalyst was added into the reactor with vigorous stirring (900 rpm) to initiate polymerization. After a prescribed time, ethanol (10 mL) was added to terminate the polymerization reaction. The resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol and acetone, and dried at 60 °C for 24 h in a vacuum oven.

Table 1
Copolymerization of ethylene/polar comonomers protected with different alkyaluminums.[a]

Entry	Cat. (μmol)	Comonomer	AlR_3[b]	Yield (g)	Activity[c]	Incorp.[d] (mol%)	T_m[e] (°C)	M_W[f] ($\times10^{-3}$)	M_W/M_n[f]
1	**1**(1.0)	10-undecen-1-ol	TIBA	0.33	1.98	2.2	115	14.9	1.8
2	**1**(1.0)	10-undecen-1-ol	TEA	0.54	3.24	2.3	116	8.90	1.9
3	**1**(1.0)	10-undecen-1-ol	TMA	1.39	8.34	2.5	117	9.00	2.0
4	**1**(1.0)	10-undecen-1-ol	DEAC	1.62	9.72	3.7	112	13.3	2.0
5	**1**(1.0)	5-hexen-1-ol	DEAC	1.42	8.50	2.7	122	14.4	2.1
6	**1**(1.0)	3-buten-1-ol	DEAC	0.65	3.90	0.4	128	16.9	1.9
7	**2**(1.0)	10-undecen-1-ol	DEAC	1.45	8.70	4.0	111	8.90	2.0
8	**3**(1.0)	10-undecen-1-ol	DEAC	1.86	11.2	3.4	113	11.7	2.0
9[g]	**4**(1.0)	10-undecen-1-ol	DEAC	Trace	–	–	–	–	–
10[g]	**4**(5.0)	10-undecen-1-ol	DEAC	0.20	0.24	2.5	115	10.5	2.0

[a] Reaction conditions: 1 μmol catalyst, DEAC/V (molar ratio) = 4000, ETA/V (molar ratio) = 500, 0.1 mol/L comonomer, V_{total} = 50 mL, 1 atm ethylene pressure, at 50 °C in toluene for 10 min.

[b] 1.0 equivalent of alkylaluminums to comonomer added as protecting reagents.

[c] Activity in $kg/mmol_v$ h.

[d] Comonomer incorporation determined by ^{1}H NMR.

[e] Determined by DSC.

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

[g] MMAO as cocatalyst.

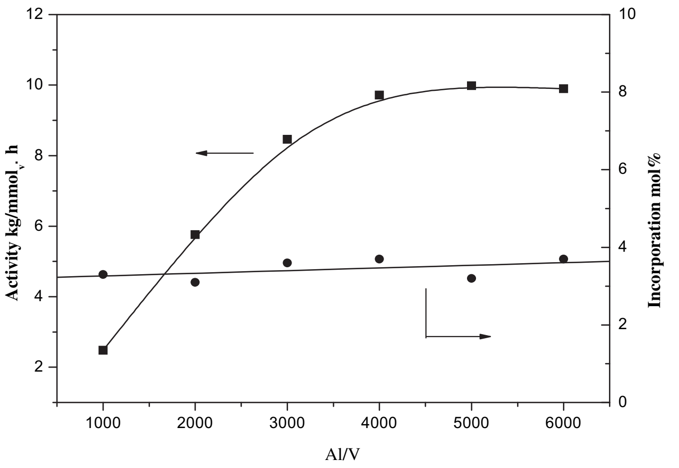


Fig. 1. Variation of catalytic activity and 10-undecen-1-ol incorporation versus Al/V mole ratio (1.0 μmol catalyst, 0.1 mol/L 10-undecen-1-ol, ETA/V = 500, 50 °C, 1 atm ethylene pressure, 10 min, $V_{total} = 50$ mL).

3. Results and discussion

Three vanadium(III) complexes bearing [N,O] ligands ([PhN=C(CH$_3$)CH=C(Ph)O]VCl$_2$(THF)$_2$ (**1**), [PhN=CHC$_6$H$_4$O]VCl$_2$(THF)$_2$ (**2**) and [PhN=CHC(Ph)=CHO]VCl$_2$(THF)$_2$ (**3**)) have been chosen as the catalysts for ethylene/α-olefin-ω-ol copolymerization since they displayed excellent ability to copolymerize ethylene with α-olefin in the presence of the DEAC as a cocatalyst and ETA as a reactivating agent, affording the high molecular weight copolymers with high comonomer incorporation [34,35]. The typical metallocene catalyst *rac*-Et[Ind]$_2$ZrCl$_2$ (**4**) was also investigated for comparison. The steric protection of the functional group through alkylaluminum has been proved to be a successful method for the prevention of catalyst deactivation [14,20]. Thus we examined the effect of alkylaluminums as monomer masking reagent on the copolymerization behaviors using catalyst **1**. Various alkylaluminums such as TiBA, TEA, TMA and DEAC were employed due to its different Lewis acidity and steric bulkness for Al center. The representative results are summarized in Table 1. The catalytic activity and monomer incorporation in the resultant copolymers increased in the order: TiBA < TEA < TMA < DEAC, which was in line with the increasing Lewis acidity of aluminum centers. The highest activity (9.72 kg/mmol$_v$ h of catalyst **1**) and 3.70 mol% incorporation of 10-undecen-1-ol were obtained when DEAC was used as monomer masking reagent. The data listed in Table 1 show that both DEAC and TiBA offered relative high molecular weight polymers than TEA and TMA, which indicated that the frequency of the chain transfer to both DEAC or TiBA was less than that to TEA or TMA under the similar conditions. In terms of high catalytic activity and efficient comonomer incorporation, therefore, DEAC was more suitable monomer masking reagent for ethylene/10-undecen-1-ol copolymerization. This is different from the case of metallocene copolymerizing ethylene with α-olefin-ω-ol, in which TiBA produced the highest molecular weight copolymers with high comonomer incorporation than the others.

The data listed in Table 1 indicated that the capabilities of the three vanadium catalysts to copolymerize ethylene with the functional α-olefin were comparable one another and only slightly depended on ligand structure. The catalytic activities of catalysts **1**–**3** towards the copolymerization were 9.72, 8.70 and 11.2 kg/mmol$_v$ h, respectively, while the corresponding 10-undecen-1-ol incorporations of the resultant copolymers were 3.70, 4.00 and 3.40 mol%, respectively, under the same conditions. Noticed that only trace copolymer was obtained by typical metallocene catalyst **4** under the same conditions (entry 9), and even increasing zirconium catalyst dosage from 1.0 to 5.0 μmol only low activity (1.2 kg/mmol$_{Zr}$ h) and 10-undecen-1-ol incorporation (2.5 mol%) were observed (entry 10), maybe since zirconium catalyst possesses higher oxophilicity than vanadium one. This result also suggested that the central metals properties of catalysts played a very important role in promoting the copolymerization of ethylene with the functional α-olefin.

The copolymerizations of ethylene with other α-olefin-ω-ol by the vanadium(III) catalysts have also been investigated. It was found that catalyst **1** can also copolymerize efficiently ethylene with 5-hexen-1-ol, and a high catalytic activity (8.50 kg/mmol$_v$ h) and a mild monomer incorporation of 2.7 mol% were obtained under the same conditions used-above (entry 5). As expected, further decreasing the length of the methylene spacers in comonomer made the copolymerization took place with much difficulty. A significant decrease in both catalytic activity (3.90 kg/mmol$_v$ h) and monomer incorporation (0.6 mol%) was detected when 3-buten-1-ol was used as comonomer because the additional steric bulkness provided by the alkylaluminum species might inhibit comonomer to incorporate into polymer chains [28]. All the copolymers obtained by catalysts **1**–**3** displayed unimodal distribution ($M_w/M_n = 1.9$–2.0), indicated that the copolymerization by **1**–**3**/DEAC catalytic systems took place with single active species.

Table 2
The copolymerization of ethylene/10-undecen-1-ol with **1**/DEAC catalysts systems.[a]

Entry	Al/V (molar ratio)	Temp. (°C)	Comonomer mol/L	Yield (g)	Activity[b]	Incorp. [c] (mol%)	T_m[d] (°C)	M_w[e] ($\times 10^{-3}$)	M_w/M_n[e]
1	500	50	0.10	0.12	0.72	3.2	114	40.8	3.5
2	1000	50	0.10	0.42	2.48	3.3	112	13.6	2.0
3	2000	50	0.10	0.96	5.76	3.1	113	13.3	1.9
4	4000	50	0.05	2.13	12.8	1.5	121	19.7	1.9
5	4000	50	0.10	1.62	9.72	3.7	112	13.3	2.0
6	4000	50	0.20	1.05	6.30	5.0	102	10.4	2.0
7[f]	4000	50	0.50	0.65	0.78	13.9	–	4.10	1.8
8	4000	20	0.10	0.64	3.84	1.4	119/128	177.1	5.4
9	4000	40	0.10	1.67	10.0	2.9	116	17.6	2.0
10	4000	60	0.10	1.22	7.32	4.0	111	7.50	1.9

[a] Reaction conditions: 1 μmol catalyst **1** (except for entry 7), ETA/V (molar ratio) = 500, $V_{total} = 50$ mL, 1 atm ethylene pressure, copolymerization in toluene for 10 min, AlEt$_2$Cl added as protecting reagents (1.0 equiv.).

[b] Activity in kg/mmol$_v$ h.

[c] Comonomer incorporation determined by ^{1}H NMR.

[d] Determined by DSC.

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

[f] 5 μmol Catalyst **1**.

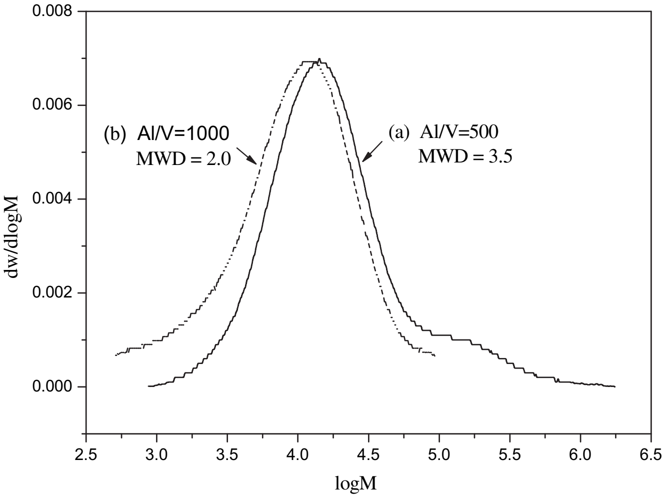


Fig. 2. Molecular weight distributions determined by GPC for the ethylene and 10-undecen-1-ol copolymers produced by catalysts 1. (1.0 μmol catalyst, 0.1 mol/L 10-undecen-1-ol, ETA/V = 500, 50 °C, 1 atm ethylene pressure, 10 min, V_{total} = 50 mL).

In order to incorporate more functional α-olefin into the polymer chains, we examined the effect of the reaction parameters on the copolymerization of ethylene with 10-undecen-1-ol. As shown in Fig. 1, the activity of catalyst **1** gradually enhanced (from 2.3 to 9.7 kg/mmol$_V$ h) with increasing Al/V molar ratio from 1000 to 4000, and then almost kept fixed, while the comonomer incorporation was independent of cocatalyst dosage under the conditions used, which indicated that the Al/V molar ratio was not an important factor to control the incorporation of 10-undecen-1-ol. The molecular weight of the resultant polymer produced by catalyst **1** decreased with the increase of Al/V molar ratio, which indicated that chain transfers to aluminum compounds existed in these systems during the copolymerizations (entries 1–3 in Table 2). In addition, the relative narrow MWD copolymers were obtained suggesting that a certain excessive amount of DEAC was necessary to maintain narrow MWD in this catalyst system, as shown in Fig. 2. Furthermore, ^{13}C NMR spectra revealed no signal of terminal vinyl in the copolymers, which also supported the above suggestion thatthe dominant chain-transfer would be chain-transfer to aluminum.

As shown in Fig. 3, reaction temperature also affected significantly catalytic activity towards the copolymerization and comonomer incorporation. With an increase of the reaction temperature, the catalytic activity rapidly enhanced and reached the highest value at 45 °C, and then gradually decreased. This result was an interesting phenomenon which was contrast to that found in the copolymerization by metallocene catalysts, in which catalysts displayed high catalytic activities at low temperature [28]. It was noticeably that the functional α-olefin incorporation was also improved with the temperature. For example, 10-undecen-1-ol incorporation approached 4.0 mol% if the copolymerization was carried out at 60 °C, which was almost 3 times higher than that obtained at 20 °C. It is noteworthy that two melting temperatures (T_m) were detected for the copolymer obtained at 20 °C (entry 8 in Table 2), and the GPC curve showed that the resultant copolymer possessed rather high MW (M_w = 177.1 kg/mol) with broad MWD (M_w/M_n = 5.4). There appeared no clear reason at this moment why **1** afforded the copolymer with bimodal MWD at low temperature. One possible explanation was that the chain transfer reactions had higher activation energy than insertion reaction. Consequently, a change in reaction temperature significantly influenced the rate of chain transfer, which in turn affected the characteristics of the resultant polymers, as reported in literature [33].

As shown in Fig. 4, the activity of catalyst **1** towards the copolymerization and comonomer incorporation were considerably influenced by the comonomer feed ratios. With an increase in the quantity of the functional α-olefin charged up to 0.5 mol/L, the 10-undecene-1-ol contents of the copolymers linearly enhanced up to 13.9 mol%, but the catalytic activity sharply decreased. The decline of catalytic activity might be ascribed to both the low insertion speed of the polar monomer and the last-inserted functional α-olefin suppressing ethylene coordination and insertion. Similarly, the MWs of the resultant copolymers also decreased upon increasing 10-undecen-1-ol concentration in the feed (entries 4–7 in Table 2) due to low rate of propagation reaction to chain transfer, but the MWDs of the resultant polymers almost kept fixed all the way. In addition, DSC analysis showed that the melting temperature of the resultant polymers gradually decreased with increase of initial 10-undecen-1-ol concentration in the feed and only one melting temperature was observed, indicating that resultant copolymer possessed uniform 10-undecen-1-ol incorporation. We evaluated the reactivity ratios of two comonomers in copolymerizations by the Fineman–Ross method [49]. The reactivity ratio products r_1r_2 = 0.83 (where

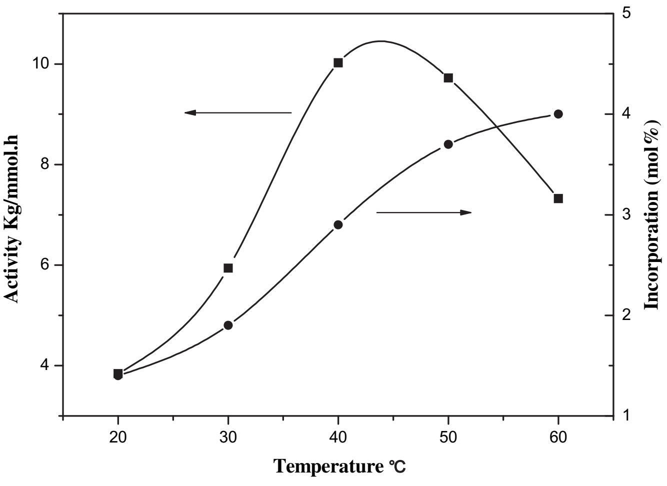


Fig. 3. Variation of catalytic activity and 10-undecen-1-ol incorporation versus reaction temperature (1.0 μmol catalyst, 0.1 mol/L 10-undecen-1-ol, Al/V = 4000, ETA/V = 500, 1 atm ethylene pressure, 10 min, V_{total} = 50 mL).

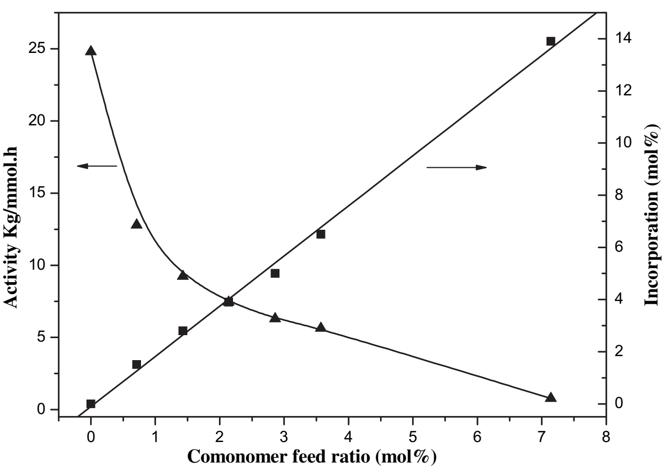


Fig. 4. Variation of catalytic activity and 10-undecen-1-ol incorporation versus comonomer feed ratio (1.0 μmol catalyst, Al/V = 4000, ETA/V = 500, 50 °C, 1 atm ethylene pressure, 10 min, V_{total} = 50 mL).

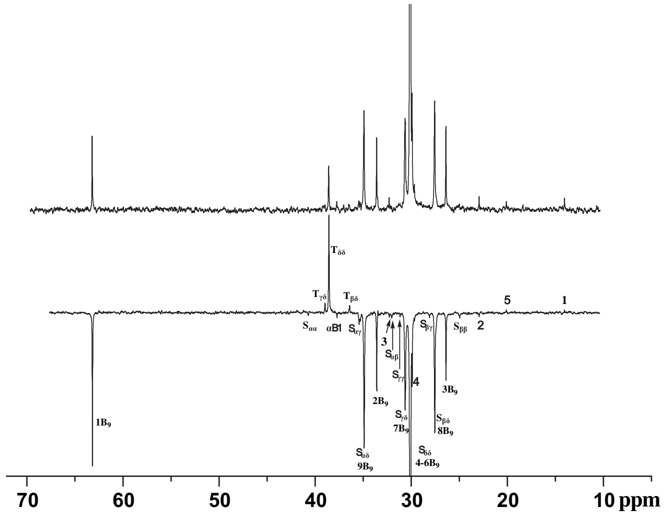


Fig. 5. Typical ^{13}C NMR and DEPT 135 spectrum of the ethylene/10-undecen-1-ol copolymers obtained with complex **1** (entry 7 in Table 2).

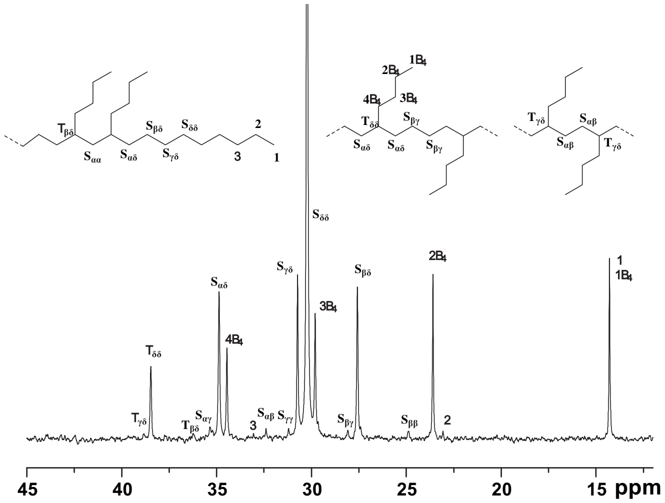
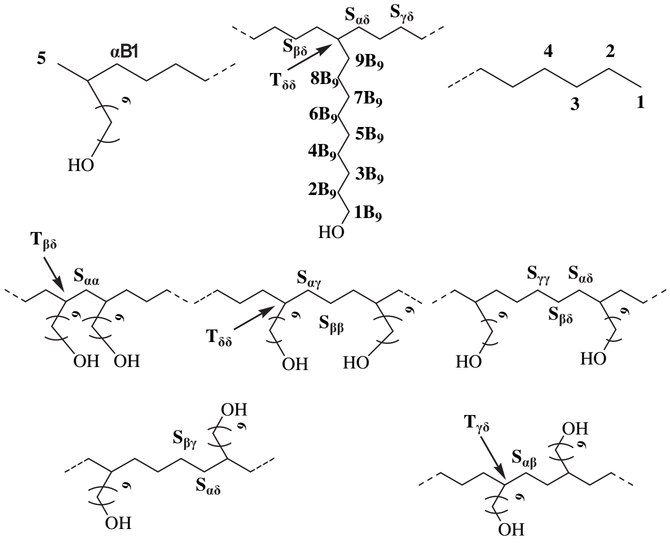


Fig. 6. Typical ^{13}C NMR spectra for ethylene/1-hexene copolymers obtained with complex **1** (1.0 μmol catalyst, 3 mL 1-Hexene, Al/V = 4000, ETA/V = 400, 50 °C, 1 atm ethylene pressure, 10 min, $V_{total} = 50$ mL).

$r_1 = 41.4$ is the reactivity ratio of ethylene, and $r_2 = 0.02$ is the reactivity ratio of the comonomer) for ethylene/10-undecen-1-ol copolymerizations was smaller than 1, and this indicated the formation the copolymers with random sequence distributions.

Fig. 5 exhibited a typical ^{13}C NMR spectrum in poly(ethylene-*co*-10-undecen-1-ol) (entry 7 in Table 2, in *o*-$C_6D_4Cl_2$ at 110 °C), and all resonances were identified by the dept analysis as well as by comparison with poly(ethylene-*co*-10-undecen-1-ol)s reported previously [8,17,18]. The ^{13}C NMR displayed that one polymer chain end group was *n*-alkyl (labeled as 1–4), and the other chain end group was methyl (labeled as 5) caused by the polymer chain transfer to alkylaluminum after the insertion of 10-undecen-1-ol. Besides chain end, 10-undecen-ol was also incorporated into the inner site of polymer chain due to the resonances of methine (labeled as $T_{\beta\delta}$, $T_{\gamma\delta}$, $T_{\delta\delta}$) appeared. The possible monomer sequences in the poly(ethylene-*co*-10-undecen-1-ol)s were summarized in Scheme 2. The resultant copolymer possessed isolated 10-undecen-1-ol inserted unit (assigned as $T_{\delta\delta}$) among the repeated ethylene insertions, and the alternating sequence (assigned as $S_{\beta\beta}$) was also present with a low extent. The resonances ascribed to (head-to-tail) two 10-undecen-1-ol repeating unit ($T_{\beta\delta}$, $S_{\alpha\alpha}$) were seen in the spectrum, but no peaks due to three monomer repeating units were observed. In addition, a trace amount of resonances due to so-called pseudo random ($S_{\alpha\beta}$, $S_{\beta\gamma}$ and $T_{\gamma\delta}$) sequences was present. To the best of our knowledge, such a regioselectivity of emerging inverse insertion of polar monomers has never been reported in the literature. The typical ^{13}C NMR spectra for poly(ethylene-*co*-1-hexene)s obtained by complex **1** provided additional evidence to confirm the regioselectivity sequence above. As shown in Fig. 6, the signals at 28.0 ppm ($S_{\beta\gamma}$), 32.5 ppm ($S_{\alpha\beta}$) and 38.9 ppm ($T_{\gamma\delta}$) caused by the inverse insertion sequences of 1-hexene were also found in the spectra [50,51], which provided strong support for the present of inverse insertion sequences of the comonomer.



Scheme 2. Possible monomer sequences in poly(ethylene-*co*-10-undecen-1-ol)s.

4. Conclusions

The copolymerizations of ethylene with polar α-olefins having an hydroxyl group, such as 10-undecen-1-ol, 5-hexen-1-ol and 3-butylene-1-ol, were investigated by three vanadium(III) catalysts bearing bidentate [N,O] ligands. The tolerance of catalysts to addition of the α-olefin-ω-ols was greatly improved when the comonomer was pretreated with alkylaluminums. In this treatment, DEAC was more suitable monomer masking reagent for copolymerization. The catalytic activity, comonomer incorporation, and the molecular weights of the copolymers could be controlled over a wide range by the variation of the reaction parameters such as Al/V molar ratio, comonomer concentration, and reaction temperature. The high 10-undecen-1-ol incorporation of 13.9 mol% could be obtained. The microstructures of copolymer and then the mechanism of the chain transfer reaction were investigated by ^{13}C NMR spectra. Polar units were located both on the main chain and at the chain end. The resultant copolymer possessed isolated 10-undecen-1-ol inserted unit among the repeated ethylene insertions, the alternating sequence and a trace amount of two 10-undecen-1-ol repeating unit in the copolymer. The reactivity ratio products $r_1r_2 = 0.83$ for ethylene/10-undecen-1-ol copolymerizations was smaller than 1, indicating the formation the copolymers with random sequence distributions. In addition, the signals derived from polar monomer inverse insertion were detected for the first time. Chain-transfer to alkylaluminum was the dominant chain-transfer pathway in the copolymerization. As far as we know, the present catalyst system was a rare example for affording functional copolymers of high comonomer incorporations with significant catalyst efficiency using homogeneous vanadium(III) complexes.

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