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# Synthesis and olefin homo- and copolymerization behavior of new vanadium complexes bearing [OSSO]-type ligands

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**Abstract** Novel vanadium complexes bearing [OSSO]-type ligands having two phenolato units linked through the $-CH_2S(CH_2)_4SCH_2-$ (**1V**) or $-CH_2S(CH_2)_2SCH_2-$ (**2V**) bridge are synthesized with good yields by reacting a deprotonated ligand with $VCl_4$. They are then used in ethylene (co)polymerization after activation with $EtAlCl_2$ and $Et_2AlCl$. In the presence of $EtAlCl_2$, both complexes promote ethylene polymerization with very high activities, over $4 \times 10^7$ g/(mol h), leading to PEs with high molecular weight and narrow molecular weight distribution. The prepared complexes exhibit lower activity for ethylene/1-octene copolymerization. It is also revealed that the catalyst based on the $-CH_2S(CH_2)_4SCH_2-$ bridged complex shows both higher activity and higher comonomer incorporation ability than the catalyst based on the $-CH_2S(CH_2)_2SCH_2-$ bridged complex. Upon activation with $Al(iBu)_3/Ph_3CB(C_6F_5)_4$, complex **2V** produces stereo- and regioirregular poly(1-octene), while **1V** gives the isotactically enriched product.

**Keywords** Vanadium complex · [OSSO]-ligand · Ziegler–Natta polymerization · Polyolefins · Copolymers

## Introduction

Developing new olefin polymerization catalysts on the basis of transition metal complexes with various ligands makes one of the most interesting areas of chemical research in recent years. Amongst such complexes, those of transition metals of group 4 with [ON] or [ONNO] ligands offer the most interesting properties [1–4]. For example, catalysts based on phenoxy-imine complexes may be not only more

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active than the metallocene catalysts, but they make it possible to produce a variety of polyolefinic materials, inclusive of ultra-high-molecular-weight PEs, well-defined multimodal PEs, selective vinyl- and Al-terminated PEs, isotactic and syndiotactic PPs, as well as stereo- and regioirregular high-molecular weight poly(1-olefin)s [1]. Group 4 transition metal complexes which incorporate tetradentate [OSSO]-type bis(phenolate) ligands have also been quite extensively studied in homo- and copolymerization of olefins as well as in polymerization of styrene and its derivatives, and in olefin-styrene copolymerization [5–18]. The titanium complex of the tetradentate [OSSO]-type diphenolate ligand with the 1,4-dithiabutanediyl-bridge yielded isotactic PS at very high activity. Polystyrene materials with the same microstructures were produced by Zr and Hf complexes bearing the identical ligand but with low yields [8]. On the other hand, titanium complexes with the longer and more flexible 1,5-dithiapentanediyl bridge promote syndiospecific styrene polymerization with relatively low activity [11]. The metal center is also important for ethylene polymerization promoted by [OSSO]MCl$_2$/MAO (M = Ti, Zr) catalysts [9]. The zirconium complex produced exclusively oligomers with even numbers of carbon atoms while its titanium analogue gave branched polymers [9, 12]. Another zirconium complex as well as the hafnium one, having a ligand bearing trans-1,2-cyclooctanediylbis(thio) core, were highly active in 1-hexene polymerization providing highly isotactic poly(1-hexene) [15, 16]. It was also shown that the regioselectivity during 1-hexene oligomerization switched when the titanium metal center was replaced with its heavier homolog (Zr, Hf) [10]. The dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium complex activated by MAO catalyzed olefin/styrene copolymerization and produced relatively high molecular weight ethylene/styrene copolymers with high styrene contents [6] and multiblock copolymers which contained long isotactic styrene sequences interrupted by short isotactic propylene strings [7]. That catalyst was also active in the copolymerization of conjugated dienes with ethylene and provided prevailingly alternating copolymers [13], in the copolymerization of ethylene with 4-methyl-1,3-pentadiene [17], and it catalyzed the homopolymerization of conjugated dienes as well [18]. Enantiomerically pure titanium complexes which contained trans-1,2-cyclohexanediyl-linked [OSSO]-type bis(phenolate) ligand were found to produce low-molecular-weight homochiral isotactic oligostyrenes which showed optical activity [14]. There are also known group 4 metal complexes with *o*-carborane-bridged [OSSO]-type tetradentate ligands with high activity towards ethylene homo- and copolymerization [19]. In contrast to group 4 elements, the group 5 complexes bearing [OSSO]-type bis(phenolate) ligands are rare [20, 21]. The oxovanadium(V) complex in conjunction with MAO showed high activity in ethylene polymerization but did not catalyze the propylene and styrene polymerization [20], and the tantalum(V) complex activated with Al(*i*Bu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ gave isotactic poly(1-hexene) with narrow dispersity [21].

The design and synthesis of new vanadium complexes which bear other chelating ligands attract however more and more interest recently [22–30]. It results from the interesting catalytic properties of this type of catalysts. Classical vanadium catalysts are able to produce high molecular weight polymers with narrow molecular weight distributions, high molecular weight amorphous ethylene/propylene copolymers,

syndiotactic propylene [22, 31, 32]. The problem of using vanadium catalysts is their rapid deactivation associated with reduction of catalytically active vanadium species to inactive vanadium(II) species, especially at higher temperatures [22, 23, 31, 32]. Adding chelating ligands to the vanadium compound can help in stabilizing the vanadium species at a high oxidation state [31]. Furthermore, the catalytic properties of the vanadium complex can be modified by the structure of the ligand used.

Within this study, new vanadium(IV) complexes were synthesized with the [OSSO]-type ligands, wherein the phenolate rings were bridged by the structure – $CH_2S(CH_2)_nSCH_2$– (n = 2 or 4), and their catalytic performance was verified in the ethylene and 1-octene polymerization processes, as well as in the copolymerization of those monomers. Moreover, the obtained products were analyzed in detail.

## Experimental part

All manipulations of air-sensitive and/or moisture-sensitive compounds were performed under an inert atmosphere, using standard Schlenk techniques and a glove box.

### Materials

Argon (grade 5.0, Air Liquide), $Et_2AlCl$ (1.0 M, Sigma-Aldrich), $EtAlCl_2$ (1.0 M, Sigma-Aldrich), $Al(iBu)_3$ (1.0 M, Aldrich), $Ph_3CB(C_6F_5)_4$ (min. 97%, Strem Chemicals), NaH (60%, Sigma-Aldrich), $VCl_4$ (Sigma-Aldrich), 1,4-butanedithiol (98%, Sigma-Aldrich), 1,2-ethanedithiol (>90%, Sigma-Aldrich) were used as received. THF and hexane were refluxed over sodium/benzophenone and then distilled, and toluene was refluxed over sodium and distilled. 1-Octene (98%, Sigma-Aldrich) and dichloromethane were dried under argon over 4A molecular sieves. Ethylene (grade 3.5, Linde Gas) and nitrogen (Messer) were used after having been passed through a column with sodium metal supported on $Al_2O_3$.

### General methods

The infrared spectra were recorded with the Nicole Nexus 2002 FT-IR spectrometer with a constant spectral resolution R = 2 $cm^{-1}$ and were taken over the spectral range 4000–400 $cm^{-1}$. Each sample was scanned 20 times. The samples of ligands and complexes were prepared under the inert atmosphere as a suspension in Nujol. Samples of (co)polymers were tested as a disk with KBr. The comonomer incorporation was determined using the modified IR method and the equation: 1-Oct (mol%) = 1.7211 $(A_{CH3}/A_{CH2})_s^2$ + 4.0123 $(A_{CH3}/A_{CH2})_s$ −0.0029 [33]. The ^{1}H NMR and ^{13}C NMR spectra were recorded with the 400 MHz Ultrashield Bruker spectrometer. The ethylene/1-octene copolymers were analyzed in 1,2-dichlorobenzene-$d_4$ at 120 °C. The samples of poly(1-octene)s and ligands were dissolved in $CDCl_3$ and their analyses were performed at room temperature. The melting temperatures ($T_m$) and crystallinity ($\chi$) of polymers were determined by differential

scanning calorimetry with a 2010 DSC calorimeter from TA Instruments at the heating rate 10 °C/min. Gel permeation chromatography was used for the determination of polymer molecular weights and molecular weight distributions. Analyses were performed using an Alliance 135 GPCV 2000 apparatus equipped with HT 3 and HT 6E columns at 135 °C using 1,2,4-trichlorobenzene (1.0 mL/min) as a solvent. The calibration curve was obtained with a narrow dispersity polystyrene standards having molecular weight range of 1000–3.7 × 10^6 g/mol.

### Synthesis of the ligand precursor $H_2L^1$

A two-neck round bottom flask was charged sequentially with THF (30 mL), 2,4-di-*tert*-butyl-6-hydroxymethylphenol (2.00 g, 8.46 mmol), 1,4-butanedithiol (0.16 mL, 4.23 mmol) and $H_2SO_4$ (1 mL). The obtained clear, light yellow solution was stirred for 24 h and then 100 mL of water was added. After the evaporation of THF, the product was extracted by methylene chloride. The extract was dried over anhydrous $MgSO_4$ and then evaporated. The dry residue (2.68 g) was crystallized from $MeOH/H_2O$. A precipitate was collected by filtration, and then dried in vacuo. 1.63 g (69%) of a white solid was obtained.

### Synthesis of the ligand precursor $H_2L^2$

Ligand precursor $H_2L^2$ was synthesized according to the method described for $H_2L^1$. Synthesis was conducted with 2.00 g (8.46 mmol) of 2,4-di-*tert*-butyl-6-hydroxymethylphenol and 0.38 mL (4.23 mmol) of 1,2-ethanedithiol. 1.75 g (77%) of a white solid was obtained.

### Synthesis of complex 1V

To a stirred colorless solution of ligand precursor $H_2L^1$ (0.50 g, 0.91 mmol) in dry THF (50 mL), 0.073 g of NaH (60% in oil, 1.82 mmol) was added. After 2 h, to the reaction mixture solution of $VCl_4$ (0.94 mmol) in toluene (5 mL) was added dropwise and it was stirred for next 4 h. The solution turned dark green and a precipitate was formed. The precipitate was filtered and dried in vacuum to an oily residue. The resulting oil was dissolved in dry methylene chloride/hexane mixture (10 mL/10 mL) and the solution was put into a freezer overnight. A precipitate was collected by filtration and dried under reduced pressure to give 0.43 g (69%) of a dark blue-green solid.

### Synthesis of complex 2V

Vanadium complex **2V** was synthesized according to the method described for **1V**. Reaction was carried out in THF (50 mL) using 0.70 g (1.32 mmol) of $H_2L^2$, 0.106 g (2.64 mmol) NaH and 0.14 mL (1.32 mmol) $VCl_4$. **2V** was obtained as a dark blue-green powder in 77% (0.66 g) yield.

## Ethylene homo- and copolymerization procedure

Ethylene (co)polymerization was carried out in a Büchi glass autoclave equipped with the magnetic stirrer and heating–cooling jacket. The required amounts of solvent (150 mL of hexane), 1-octene (in case of copolymerization) and the activator were introduced into the reactor following this order. Then, after the prescribed temperature was reached, the toluene solution of complex was added. (Co)polymerization was started after introducing ethylene and the pressure was kept constant at 5 bar throughout the reaction time. Termination was performed by venting the reactor and transferring the obtained mixture to a dilute solution of hydrochloric acid in methanol. The polymer was filtered, washed a few times with methanol and dried initially in air and then in vacuum oven.

## 1-Octene polymerization procedure

1-Octene polymerization was carried out in a two-neck 100 mL flask equipped with a magnetic stirrer. First the monomer, and then $Al(iBu)_3$, the vanadium complex and last $Ph_3CB(C_6F_5)_4$ were introduced into the flask. The mixture was stirred for the prescribed time. The reaction was terminated by adding the acidified methanol. The obtained polymer was washed with methanol and dried in air and then in vacuum oven at 45 °C.

## Result and discussion

### Synthesis of ligands and complexes

By reacting 2,4-di-*tert*-butyl-6-hydroxymethylphenol with 1,4-butanedithiol and with 1,2-ethanedithiol (Scheme 1), two [OSSO]-type ligands were synthesized with different numbers of $CH_2$ groups in the bridge which linked the donor sulfur atoms. The yield of synthesis reached 69% for $H_2L^1$ and 77% for $H_2L^2$. The $^1H$ NMR
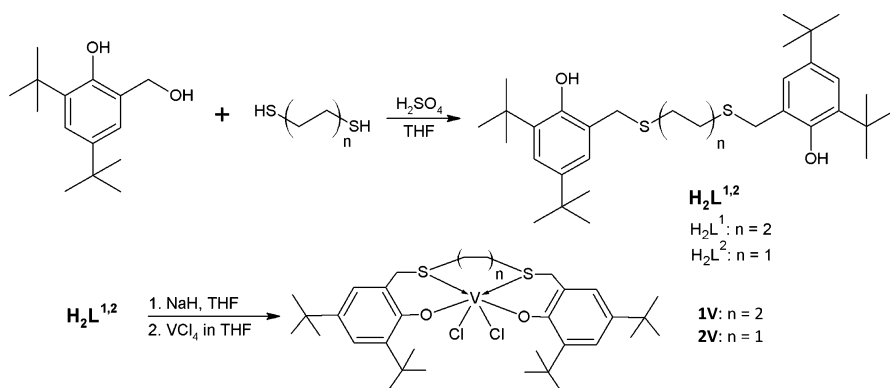


**Scheme 1** Synthesis of ligands and their vanadium complexes

spectra of those ligands (Fig. 1) reveal signals for *tert*-butyl groups (1.28 and 1.41 ppm as well as 1.26 and 1.41 ppm in the $H_2L^1$ and $H_2L^2$ spectra, respectively), the proton signal of the groups $ArCH_2S$ (3.78 and 3.75 ppm in the $H_2L^1$ and $H_2L^2$ spectra), two doublets at 6.90 and 7.26 ppm as well as 6.89 and 7.26 ppm in the $H_2L^1$ and $H_2L^2$ spectra, respectively, which come from aromatic protons, and the proton signal of hydroxyl groups, which was observed in the spectra of those ligands at 6.72 and 6.50 ppm. Moreover, two signals can be seen in the spectrum for the ligand $H_2L^1$, at 1.57 ppm and at 2.34 ppm for the protons of the $CH_2$ groups in the butylene bridge, while the spectrum of the ligand with the ethylene bridge shows a signal at 2.56 ppm, which can be ascribed to the ethylene bridge $CH_2$ protons.
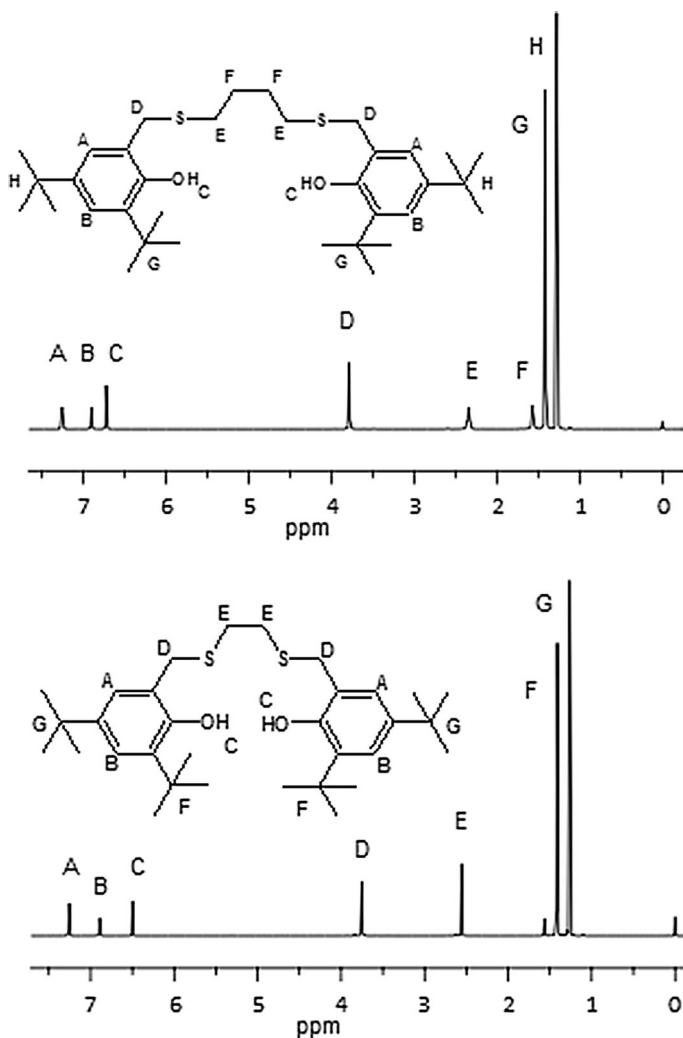


**Fig. 1** $^1H$ NMR spectra of $H_2L^1$ and $H_2L^2$

The prepared tetradentate ligand precursors were deprotonated with NaH and then they were reacted with 1.0 equivalent of $VCl_4$ in toluene. A general synthetic route for the complexes is shown in Scheme 1. After workup, the complexes were isolated as dark blue-green powders at moderate yields: 0.43 g of **1V** and 0.66 g of **2V**. Both complexes, and ligand precursors for comparison, were characterized by FTIR spectroscopy. The obtained spectra are presented in Fig. 2. As can be seen, the spectra of the complexes are different from those of the appropriate ligands, which confirms the reaction to have occurred. The bands present in the spectra of ligands at about 3262 cm$^{-1}$ ($H_2L^1$) and 3345 cm$^{-1}$ ($H_2L^2$) due to the disappearance of the stretching O–H frequencies in the spectra of the complexes. Ligands exhibit the bands at 1601, 1593 cm$^{-1}$ ($H_2L^1$) and 1603, 1591 cm$^{-1}$ ($H_2L^2$) as a result of $\nu$(C=C) vibration. These bands appear at 1612, 1593 cm$^{-1}$ (**1V**) and 1594 cm$^{-1}$ (**2V**) in the spectra of vanadium complexes. The band observed at around 1200 cm$^{-1}$ and 1196 cm$^{-1}$ in the spectra of ligands is attributed to the phenolic $\nu$(C–O) vibration and in the spectra of complexes it is seen at 1226 and 1225 cm$^{-1}$. Such changes confirm the formation of the V–O bonds. It is also confirmed by a new band, which appeared at around 480 cm$^{-1}$, which can represent the $\nu$(V–O) mode [34]. Moreover, the changed location can be observed for the band which is specific for the $\nu$(C–S) and which can be observed at 1221 and 1238 cm$^{-1}$ for ligands and at 1243 and 1246 cm$^{-1}$ for complexes [35]. The bands due to $\nu$(V–Cl) were not observed because they are usually present in the far infrared region below 400 cm$^{-1}$ [36].

## Ethylene homo- and copolymerization

The ability of the vanadium complexes to polymerize ethylene was investigated after their activation by the $EtAlCl_2$ or $Et_2AlCl$. Polymerization experiments were conducted in hexane using 0.5 μmol of the vanadium complex. The reaction temperature was set up at 30 °C since the vanadium compounds are known to readily undergo reduction to lower oxidation states which are inactive in polymerization [22, 23]. To overcome this problem, the reactivating agents are often used, even at low temperatures [23]. Few vanadium catalysts are known so far
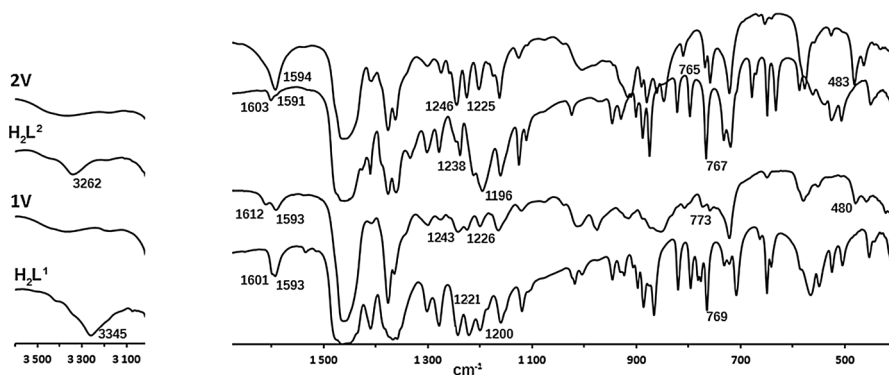


**Fig. 2** FTIR spectra of complexes **1V** and **2V** as well as corresponding ligand precursors $H_2L^1$ and $H_2L^2$

to display high thermal stability, for example (arylimido)vanadium(V) complexes with tridentate Schiff base ligands [37]. Table 1 summarizes the polymerization results and reaction conditions. Both vanadium complexes were most active when activated with EtAlCl$_2$ (entries 1 and 8). Their activities were very high, over 40,000 kg/(mol h). Besides, the activities of the studied vanadium complexes are much higher than those observed in ethylene polymerization for titanium, hafnium and zirconium complexes which contain [OSSO] ligands of different structure [12, 19], and for the vanadium(V) complex which contains a *trans*-1,2-dithiacyclohexane-bridged bis(phenolato) ligand activated with MAO [20]. After the complex amount was reduced to 0.05 μmol, the activity of the catalysts was lowered, which may result from easier reduction of vanadium to inactive oxidation states at a very high Al:V molar ratio amounting to 60,000:1, with a higher loss of activity observed for the complex **2V**. In general, the catalysts which are based on the complex having the –CH$_2$S(CH$_2$)$_4$SCH$_2$– bridge (**1V**) show a higher activity than those based on the complex with the –CH$_2$S(CH$_2$)$_2$SCH$_2$– bridge (**2V**). The opposite effect of the bridge length, e.g. lower activity for a complex bearing a longer bridge, was observed earlier for bis(phenolate) titanium complexes with 1,4-dithiabutanediyl and 1,5-dithiapentanediyl bridges [12], which may result both from different metal centres in a complex and from different ligand structures. As can be seen from Table 1, all the produced polyethylenes possess high molecular weight and high melting temperature in the range 137.3–139.9 °C. In addition, the molecular weight distribution for these polymers is very narrow (in the range of 1.4–1.7), which can suggest that the investigated catalysts are single-site in nature.

Polymerization tests were also conducted in the presence of methylaluminoxane however very low catalytic activities were obtained (e.g. the activity of **1V**/MAO was equal to 292 kg/(mol h)).

Having in mind the importance of branched polyethylenes and the lack of information about the catalytic properties of [OSSO]-type complexes (with the exception of Ti and Zr complexes with the [OSSO]-carborane ligand [19]) in the copolymerization of ethylene with 1-olefins, the ethylene/1-octene copolymerization was investigated. The copolymerization ability of both complexes was estimated after activation by EtAlCl$_2$ and Et$_2$AlCl under the same polymerization conditions: 30 min, 30 °C, 5 bar of ethylene and 3 mmol of activator. 10, 5 and 2 mL of 1-octene was used in the copolymerization, which corresponds to the ratio of the molar concentrations of 1-octene/ethylene in the feed equal 0.53, 0.27 and 0.11 (ethylene concentration under the reaction conditions was used as reported in [38]). The results are collected in Table 1. The catalytic activity of all the systems was lower for copolymerization than that for homopolymerization of ethylene. This negative "comonomer effect" is frequently observed in ethylene/1-olefin copolymerization with different catalytic systems [39]. The incorporation of 1-olefin into the copolymer at the same 1-olefin concentration depends on the catalytic system type: **1V**/Et$_2$AlCl was found to give the product with about twice higher content of comonomer than **2V**/Et$_2$AlCl (Table 1, run 7 vs. 14). In addition, the increase of ratio of the molar concentrations of the comonomers, from 0.27 to 0.53, resulted in higher 1-octene incorporation into the copolymer from 2.8 to 3.9% mol (run 6 and 7).

**Table 1** Results of ethylene polymerization and ethylene/1-octene copolymerization catalyzed by vanadium complexes having [OSSO]-type ligands

| Run | Complex | 1-Octene^e (mL) | Activator | Yield (g) | Activity^a | $T_m$ (°C) | χ (%) | 1-Oct (mol%) | $M_w \times 10^{-3}$ | $M_w/M_n$ |
|-----|---------|-----------------|-----------|-----------|------------|-----------|-------|--------------|----------------------|-----------|
| 1^b | 1V | – | EtAlCl$_2$ | 1.922 | 46,128 | 137.9 | 50.3 | – | 1273 | 1.66 |
| 2 | | 5 | EtAlCl$_2$ | 0.381 | 1524 | 112.7^c | 31.8^c | ND | ND | ND |
| 3^d | | – | EtAlCl$_2$ | 0.885 | 35,400 | 137.3 | 48.0 | – | 1232 | 1.52 |
| 4 | | – | Et$_2$AlCl | 0.382 | 1528 | 139.1 | 60.8 | – | 554 | 1.40 |
| 5 | | 2 | Et$_2$AlCl | 0.103 | 412 | 126.3 | 44.5 | ND | 1219 | 1.44 |
| 6 | | 5 | Et$_2$AlCl | 0.037 | 148 | 119.8 | 41.7 | 2.8 | 1091 | 1.37 |
| 7 | | 10 | Et$_2$AlCl | 0.024 | 96 | 113.2 | 34.8 | 3.9 | 425 | 1.39 |
| 8^b | 2V | – | EtAlCl$_2$ | 1.712 | 41,088 | 138.5 | 45.2 | – | 1043 | 1.56 |
| 9 | | 5 | EtAlCl$_2$ | 0.471 | 1884 | 113.3^c | 32.9^c | 3.5^c | ND | ND |
| 10^d | | – | Et$_2$AlCl | 0.136 | 5440 | 139.0 | 55.7 | – | 630 | 1.42 |
| 12 | | – | Et$_2$AlCl | 0.215 | 860 | 139.9 | 58.7 | – | 1144 | 1.53 |
| 13 | | 2 | Et$_2$AlCl | 0.207 | 828 | 127.2 | 46.9 | 1.0 | 1137 | 1.41 |
| 14 | | 10 | Et$_2$AlCl | 0.029 | 116 | 112.3; 128.0 | – | 1.8 | ND | ND |

Conditions: 0.5 μmol of complex, 30 min., 30 °C, 5 bar of ethylene, 3 mmol of Et$_n$AlCl$_{(3-n)}$ (n = 2 or 1), 150 mL of hexane (solvent)

1-*Oct* comonomer content in the copolymer

*ND* not determined

^a Activity, kg/(mol$_V$ h)

^b 5 min

^c Determined after removing admixture of poly(1-octene) from copolymer

^d 0.05 μmol of complex

^e 1-octene/ethylene molar ratio in the feed was equal 0.53, 0.27 and 0.11 for 10, 5 and 2 mL of 1-octene in the feed

   The obtained copolymers had different thermal and molecular properties than their corresponding polyethylenes. First of all, their melting points and crystallinity were lowered. $T_m$ and crystallinity of PE produced by **1V**/Et$_2$AlCl were equal to 139.1 °C and 60.8%, and they decreased to 119.8 °C, 41.7% and 113.2 °C, 34.8% after 5 and 10 mL of 1-octene was added to the polymerization feed, respectively (Table 1, Fig. 3). Moreover, a clear widening of the melting peaks of copolymers can be observed in DSC curves in relation to melting peaks of homopolymers, which is indicative for heterogeneity of the chemical compositions of those copolymers. Even higher heterogeneity is shown by the copolymers obtained with the use of **2V**/Et$_2$AlCl. The DSC thermogram of the copolymer 14 (Fig. 3) reveals the presence of two macromolecular fractions with highly different melting points, i.e. with different comonomer incorporation levels. It should be emphasized that the obtained copolymers are not homogeneous from the viewpoint of their chemical compositions, yet they offer very narrow molecular-weight distributions ($M_w/M_n = 1.4$), just alike ethylene homopolymers. Fig. 4 presents DSC curves for copolymers obtained with the use of both vanadium complexes activated with EtAlCl$_2$. As can be seen, those copolymers offer much lower $T_m$ values than the copolymers obtained with the use of Et$_2$AlCl at the same comonomer concentration in the reaction medium, thus at a higher incorporation level of the comonomer. Adding the comonomer to the reaction medium and increasing its concentration also resulted in lower molecular weights of copolymers, which can be accounted for by the involvement of 1-octene in the polymer chain termination reaction (Fig. 5).

   The microstructure of the copolymers was analyzed by $^{13}$C NMR spectroscopy (Fig. 6). The assignment of the peaks to specific carbon atom was made based on [40, 41]. The spectrum of poly(ethylene-co-1-octene) produced by **1V**/Et$_2$AlCl (run 6) exhibits signals at 14.05 (1s + 1B6), 22.89 (2s + 2B6), 27.35 ($\beta\delta$ + 5B6), 30.02 ($\delta\delta$+4B6), 30.50 ($\gamma\delta$), 32.22 (3B6), 34.61 ($\alpha\delta$+6B6) and 38.23 ppm (CH), indicating that the copolymer contains isolated 1-octene units. In the spectrum of copolymer 9, which was synthesized with **2V**/EtAlCl$_2$, additional peaks at 31.86 and



Fig. 3 DSC thermograms (co)polymers produced by **1V**/Et$_2$AlCl and **2V**/Et$_2$AlCl
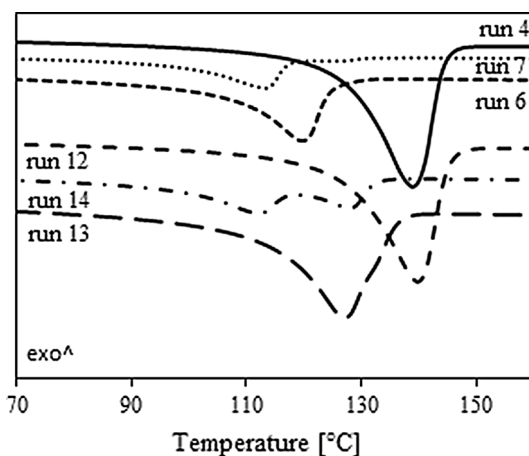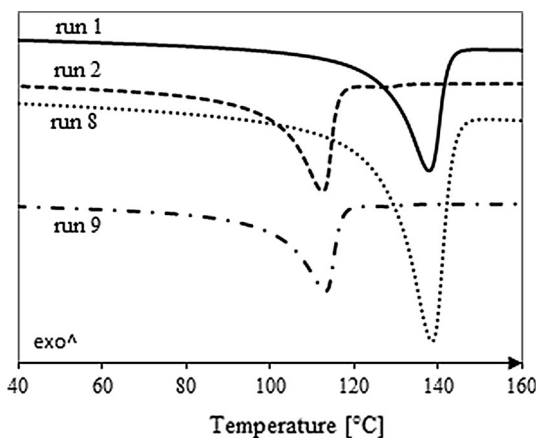
**Fig. 4** DSC thermograms (co)polymers produced by **1V**/EtAlCl$_2$ and **2V**/EtAlCl$_2$



at about 41 ppm can be seen due to the presence of αα and γγ carbon atoms, which reveals the presence of OEEO-type and blocky sequences of 1-octene units. Moreover, additional signals are present in the spectrum which may be indicative for the presence of the 1-octene homopolymer. Hence, a fraction soluble in CHCl$_3$ was separated from the copolymer and its share amounted to 38%. Its analysis by the $^{13}$C NMR method (Fig. 6c) confirmed the presence of poly(1-olefin) with branched structure according to [42].

## Polymerization of 1-octene

Both complexes in conjunction with Al($i$Bu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ were tested in 1-octene homopolymerization. As can be seen in Table 2, their activity in that reaction was very low. 1-Octene conversion was below 2% and increasing the reaction time to 6 h (run

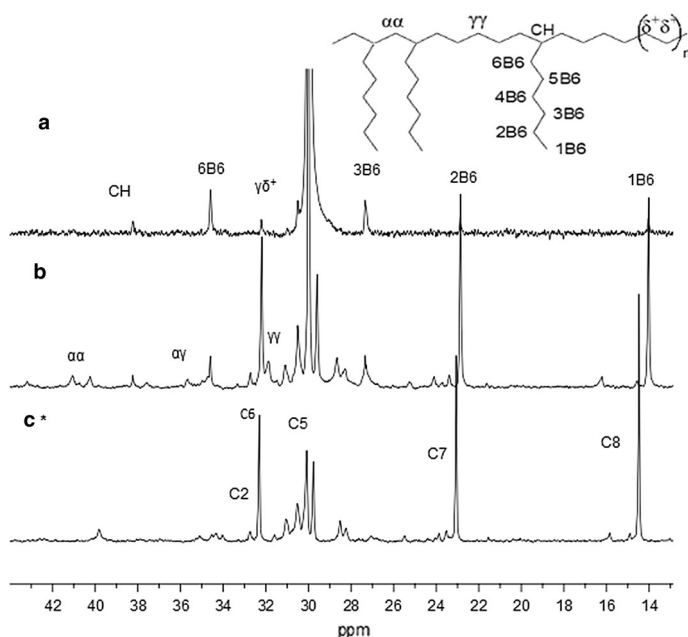**Fig. 5** GPC curves for ethylene/1-octene copolymers synthesized with **1V**/Et$_2$AlCl
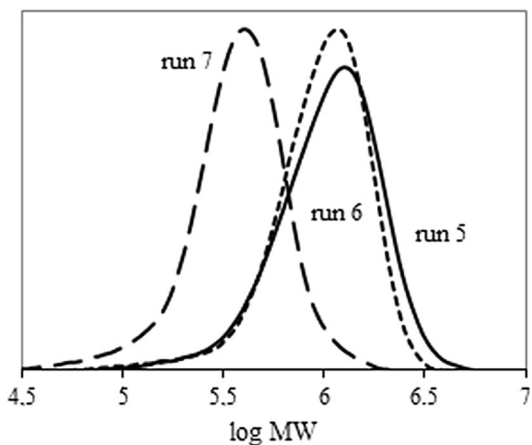
**Fig. 6** $^{13}$C NMR spectrum of ethylene/1-octene copolymer synthesized with **1V**/Et$_2$AlCl, run 6 (**a**) and **2V**/EtAlCl$_2$, run 9 (**b**) as well as polyolefin extracted from copolymer 9 (**c**)

**Table 2** Results of 1-octene polymerization catalyzed by vanadium complexes activated by Al($i$Bu)$_3$/ Ph$_3$CB(C$_6$F$_5$)$_4$

| Run | Complex | Time (min) | Yield (mg) | Conversion (%) |
|---|---|---|---|---|
| 15 | **1V** | 120 | 45 | 0.8 |
| 16 | **2V** | 120 | 93 | 1.6 |
| 17 | **2V** | 360 | 232 | 4.1 |

Conditions: 0.03 mmol of complex, 0.025 mmol of Ph$_3$CB(C$_6$F$_5$)$_4$, 0.45 mmol of Al($i$Bu)$_3$, RT (23 °C), 8 mL of 1-octene

17) raised the comonomer conversion to 4.1%. The activity of the previously studied vanadium(V) complex, [OSSO]VO(OPr), was even lower [21]. In general, the vanadium complexes reported for 1-olefin homopolymerization are very rare [43]. The microstructure of the produced polymers was characterized by $^{13}$C NMR spectroscopy. The resonances in the spectra (Fig. 7) were assigned based on earlier reports [44, 45]. The very broad signal around 35 ppm in the spectrum in Fig. 7b, which is assigned to the C3 carbon, is indicative for the atactic nature of poly(1-octene) produced by **2V**. This spectrum, apart from signals of carbon C1–C8, exhibits the additional peak at 28.5 ppm which originates from enchained regioerrors [44]. In the $^1$H NMR spectrum of that polymer, in its olefinic region, there are signals at 5.4 and
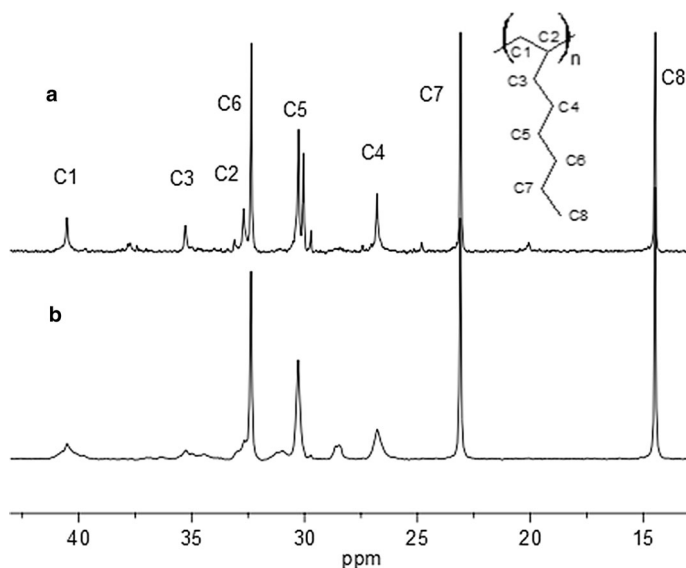
**Fig. 7** $^{13}$C NMR spectra of poly(1-octene)s obtained in run 17 (**b**) and in run 15 (**a**)

4.7 ppm due to vinylene and vinylidene end groups. The presence of those groups results from the monomolecular or bimolecular (with the monomer involved) β-H elimination, which was preceded by a growth of macromolecule via the 2,1-insertion and 1,2-insertion mechanisms, respectively. Poly(1-octene) synthesised with **1V** (Fig. 7a) is also atactic, with the share of isotactic pentad equal to 28.2%.

## Conclusions

Tetradentate [OSSO]-type ligand precursors were easily synthesized in the one pot procedure by reacting 2,4-di-*tert*-butyl-6-hydroxymethylphenol with 1,4-butanedithiol or 1,2-ethanedithiol. Using the obtained compounds, new vanadium complexes were prepared and utilized in ethylene and 1-octene homopolymerization, and in ethylene/1-octene copolymerization. In conjunction with EtAlCl$_2$, they turned out highly active in ethylene homopolymerization, over $4 \times 10^7$ g/(mol h), while its activity was lower after activation with Et$_2$AlCl, up to $1.5 \times 10^6$ g/(mol h). The produced PEs had high molecular weights and very narrow dispersity. Besides, the vanadium catalysts catalyzed ethylene/1-octene copolymerization with low activity and yielded the products with medium comonomer incorporation only. Their catalytic properties were also dependent on the complex structure. The catalyst based on the –CH$_2$S(CH$_2$)$_4$SCH$_2$– bridged complex (**1V**) showed both a higher activity and a higher comonomer incorporation ability than the complex **2V** based on the –CH$_2$S(CH$_2$)$_2$SCH$_2$– bridge. Upon activation with Al(*i*Bu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$, the complex **2V** produced stereo- and regioirregular poly(1-octene), while **1V** gave the isotactically enriched product.

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