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A comparative study on the polymerization of 1-octene promoted by vanadium and titanium complexes supported by phenoxyimine and salen type ligands

Marzena Białek · Elwira Bisz

Abstract Polymerizations of 1-octene were carried out in the presence of vanadium and titanium complexes bearing salen-type or phenoxyimine ligands activated with various co-catalysts. Vanadium complexes turned out active only in conjunction with MAO, whereas the titanium ones were active in combination with $Al(i\text{-}Bu)_3/Ph_3CB(C_6F_5)_4$. The activity of all catalysts was moderate or low and it was dependent on the ligand type: bis(phenoxyimine) complexes were more active than the salen ones. Both vanadium and titanium catalytic systems produced poly(1-octene)s possessing atactic structures with [*mmmm*] sequences in the range from 12 to 56 % at room temperature. A temperature decrease to 0.5 °C for the reaction catalyzed by the vanadium catalyst led to poly(1-octene) of [*mmmm*] = 70 %. The ^1H NMR analysis showed that unsaturated end groups were present in poly(1-octenes) which were introduced to the polymer chains as a results of various chain transfer reactions. In case of vanadium catalysts, vinylidene and vinylene end groups were present in polymer products. For titanium catalyst, vinyl and tri-substituted unsaturated groups were present in poly(1-octenes) in addition to the end groups as mentioned before.

Keywords 1-octene · Ziegler-Natta polymerization · Vanadium · Titanium · Salen ligand · Phenoxyimine ligand

Introduction

Polyethylene and polypropylene are the most important synthetic polymers with the production in the year 2000 equal to 78.7 million tons and the annual production estimated for 2010

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at about 147 million tons [1]. Other poly(α-olefin)s attract less attention thought the polymeric materials based on α-olefins polymers can find variety of applications. Low molecular weight poly(α-olefin)s can be used as base materials for lubricating oil formulation while high molecular weight products can be used as pour point depressant and drag-reducers [2]. Such application have also poly(1-octene) [3] and also it can be used in adhesives [3, 4], foams [3], carriers in antiperspirants and deodorants [3, 5].

In spite of lower interest in the higher α-olefin polymers then in polyethylene or in polypropylene, α-olefin polymerization is an important field of coordination polymerization since the discovery of Ziegler-Natta catalysts in the early 1950's. The subsequent significant progress in controlling polymerization processes brought about the development of the new classes of catalysts, metallocene ones—based on cyclopentadienyl ligands, and non-metallocene ones—with various chelating ligands. Kol et al. introduced the family of catalysts bearing dianionic tetradentate chelating ligands such as salans [6], salophan [7] and amine bis(phenolate) with an extra donor group on the side arm [8]. Those examples demonstrate the crucial role of the environment of the metal centre in tailoring the molecular weight and stereoregularity of polyolefins and catalytic activity. Salen makes another example of a tetradentate dianionic ligand. A salen ligand (salen = N,N'-bis(salicylidene) ethylenediamine) and its derivatives captured great attention over the past several years, mainly due to their applications in the field of synthesis and catalysis [9]. Complexes bearing such a type of ligand are involved in many catalytic reactions. However, their catalytic properties in the olefin polymerization processes were not fully recognized. That is true especially for the vanadium ones which were evaluated in ethylene polymerization only [10]. Zr-based salen complexes were explored in ethylene oligomerization by Zhu et al. [11], and in ethylene and propylene polymerizations by Reppo et al. [12]. Furthermore, Pellecchia et al. [13] investigated the binaphthyl-bridged Zr-based salen complex

in polymerization of propylene and α-olefins. Having in mind that the classical vanadium catalysts, although usually less active, offer the polymer products with several unique properties [14] and that the salen ligand to some extent stabilizes V species in ethylene polymerization, we evaluated the properties of the salen-type vanadium complex in 1-octene polymerization. The same studies were performed with the Ti complex for reference. Moreover, to get more information about the role of the metal centre in the polymerization mechanism, we made the comparative study on the olefin polymerization also in the presence of V and Ti complexes with phenoxy-imine ligands. Their properties in the polymerizations of α-olefins, especially those of the vanadium catalysts, have not been recognized although FI catalysts have been extensively studied for several years [15].

Experimental

General methods All air and moisture sensitive compounds were handled under argon blanketing, with the use of the standard Schlenk and glove box techniques. The DSC experiments were carried out with the 2010 DSC calorimeter from TA Instruments. The samples were heated and cooled at a rate of 10 °C/min. The infrared spectra of poly(1-octene)s were recorded on the Nicole Nexus, 2002 FT-IR spectrometer. Test samples were prepared by placing a small amount of the compound under investigation between two KBr plates. The ^1H NMR and ^{13}C NMR spectra were recorded on the Ultrashield Bruker spectrometer (400 MHz) in 1,2-dichlorobenzene-d$_4$, at 60 °C.

Materials 1-Octene (98 %, Aldrich) was dried under argon over 4A molecular sieves. Toluene was dried by refluxing over sodium. Argon (5.0 grade, Linde Gas), methylaluminoxane (MAO) (10.0 wt %, Aldrich), Et$_3$Al (25 wt %, Aldrich), Et$_2$AlCl (1.0 M, Aldrich) and EtAlCl$_2$ (25 wt %, Aldrich) were used without further purification. Salen and bis(phenoxyimine) complexes were prepared according to [10, 16]

Polymerization of 1-octene Polymerization was carried out in a two-neck 100 mL flask equipped with a magnetic stirrer, which was previously purged with argon. Required amounts of solvent (toluene), monomer (from 2 to 5 ml) and activator (MAO or common alkylaluminium compound, 3 mmol) were added to the flask at room temperature. At the prescribed polymerization temperature (in the range from 0.5 °C to 60 °C) the desired amount of catalyst, 0.03 mmol (if not specified different), was added to the reaction mixture. Time when catalyst was added, was defined as starting time of polymerization. In case of polymerization in the presence of Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ as an activator, first the solvent, monomer, Al(iBu)$_3$ (0.45 mmol, Al/M = 15), catalyst (0.03 mmol) and then Ph$_3$CB(C$_6$F$_5$)$_4$ (0.06 mmol) were introduced to the reactor. 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 under vacuum.

Results and discussion

1-octene polymerization

The salen-type vanadium and titanium complexes (Fig. 1) were synthesized according to the reported procedure [10] while bis(phenoxy-imine) was prepared in accordance with [16] by reacting the appropriate ligand with VCl$_4$ or TiCl$_4$. The complexes were characterized with the use of FTIR. Due to very low solubility of the complexes in common solvents, the NMR and X-ray analyses were not performed. The vibrations of groups ν (C=N) and ν (C–O) in the salen ligand were observed at the frequencies 1,634 cm^{-1} and 1,280 cm^{-1}, respectively. Vibrations of the group ν (C=N) in complexes were shifted to higher frequencies and they were recorded at 1,654 cm^{-1} (1Ti) and 1,655 cm^{-1} (2 V). The locations of the stretching bands ν (C–O) in complexes were also displaced and they were noted at 1,269 cm^{-1} and at 1,265 cm^{-1} in the spectra for the titanium and vanadium complexes, respectively. Similar changes were observed for bis(phenoxy-imine) complexes and for free ligands. For example, the spectra showed the following changes in locations of the ν (C=N) bands in complexes in relation to their corresponding ligands: 1,620 cm^{-1} (ligand) versus 1,647 cm^{-1} (complex 8 V); 1,615 cm^{-1} (ligand) versus 1,644 cm^{-1} (complex 7 V); 1,621 cm^{-1} (ligand) versus 1,641 cm^{-1} (complex 6 V); and 1,622 cm^{-1} (ligand) versus 1,642 cm^{-1} (complex 8Ti). Such changes are indicative for the formation of complexes.

Polymerization of 1-octene with the salen complex of vanadium was conducted with the use of EtAlCl$_2$, MAO and Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ as an activator in toluene as a solvent, at ambient temperature. The polymer was obtained only in the presence of the 2 V/MAO complex. Thus, the effects of temperature and 1-octene concentration on polymerization were studied for that catalytic system. The results were summarized in Table 1. The catalytic system displayed the activity of 1,220 g/mol$_v$ (Entry 3) at 19.1 °C after 90 min. As the temperature was decreased, the catalyst activity decreased and the molecular weight increases from 232 000 to 312 000 g/mol (Entry 3 and 15). In both cases the poly(1-octene) looked rather like a solid elastomer and not like viscous oil. The opposite effect was
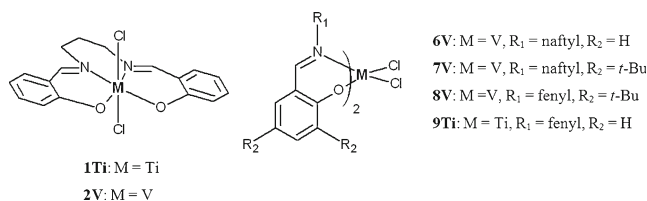

Fig. 1 Complexes applied in present work

6V: M = V, R$_1$ = naftyl, R$_2$ = H
7V: M = V, R$_1$ = naftyl, R$_2$ = t-Bu
8V: M = V, R$_1$ = fenyl, R$_2$ = t-Bu
9Ti: M = Ti, R$_1$ = fenyl, R$_2$ = H

1Ti: M = Ti
2V: M = V

observed at increased temperatures, i.e. the product was oily and its yield was higher (Entry 36). That effect was as expected because the rise of temperature usually influences the rate of elemental reactions: the propagation and chain transfer reactions are accelerated. Moreover, the polymerization was carried out at three different monomer concentrations at ambient temperature (Table 1, Entry 3, 43, 24). The catalyst productivity clearly increased with the increasing monomer concentrations and molecular weight of the products decreased. In turn, longer polymerization time leads to the growth of molecular weight of poly(1-octane) (Table 1, Entry 24, 39). The molecular weight distribution (M_w/M_n) in poly(1-octene)s synthesized with vanadium complex, independently on polymerization conditions, is very broad what implies that the polymers are produced by a multiple active species. Figure 2 (curve 1) shows a GPC traces for exemplary polymer.

For comparison and to see how the metallic centre affects the catalyst performance, 1-octene was subjected to polymerization over the salen complex of titanium. Initially, the polymerization experiments were conducted in which various activators were used, like $EtAlCl_2$, MAO and $Al(iBu)_3/Ph_3CB(C_6F_5)_4$, and then the effect of reaction parameters was verified. The results are shown in Table 1. The titanium complex was active in 1-octene polymerization only in conjunction with $Al(iBu)_3/Ph_3CB(C_6F_5)_4$ and its activity increased with the increase of the monomer concentration (Entry 12 and 31). At higher 1-octene concentration, however, oil was obtained instead of a sticky solid material. That indicates that the monomer participated in the chain transfer reaction to a high degree in case of the titanium catalyst. The investigated catalyst turned out inactive at 60 °C.

The thermal properties of synthesized poly(1-octene)s were investigated by means of differential scanning colorimetry. All polymers synthesized with the vanadium catalyst showed the glass transition from −68.4 to −69.5°, which was by over 10° higher than in case of polymers obtained with the titanium
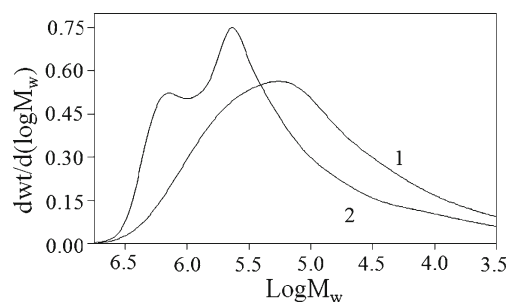

Fig. 2 GPC curves for polymers obtained with (1) - 2 V/MAO (entry 39, Table 1) and (2) - 6 V/MAO (entry 44, Table 2)

catalyst (around −81 °C). A slight difference can be seen for the vanadium-catalyzed products obtained at different temperatures. Such differences can be connected with the molecular weights of poly(1-octene)s. The T_g values decrease to follow the molecular weight decrease due to increasing flexibility of the polymer chains.

The 1-octene polymerization in the presence of bis(phenoxyimine) complexes was carried out under similar experimental conditions as for polymerizations catalyzed by salen complexes within the monomer, catalyst and activator concentrations. The related polymerization temperatures were applied as well. The results were given in Table 2. Alike for the vanadium salen complex, the vanadium complex 6 V with phenoxyimine ligands turned out inactive in 1-octene polymerization upon treatment with $Al(iBu)_3/Ph_3CB(C_6F_5)_4$. 1-Octene polymerization was possible over 6V/MAO, and the reaction productivity clearly grew up with the increase of the monomer concentration (Entry 20 and 45) and polymerization time (Entry 45, 25, 44, 46 and 50). Similarly to the vanadium catalyst with salen-type ligand, the bis(phenoxyimine)vanadium catalyst gives poly(1-octene)s of high M_w, which was dependent on polymerization time (M_w was equal to 204 000 g/mol and 576 000 g/mol for

Table 1 Results of 1-octene polymerization with complex 2 V/MAO and complex 1Ti/ $Al(iBu)_3/Ph_3CB(C_6F_5)_4$

Entry	Catalyst	Monomer [mol/dm³]	Time [min]	T [°C]	Yield [mg]	Productivity [g/mol$_M$]	C[b] [%]	T_g [°C]	[mmmm] [%]	M_w [g/mol]
1	2 V/MAO [a]	1.83	85	20.5	17.9	1,200	0,63	nd	12	nd
15	2 V/MAO	2.01	90	1.0	14.6	487	0.51	−68.5	nd	312 000
3	2 V/MAO	2.01	85	19.1	36.6	1,220	1.28	−69.5	nd	232 000
36	2 V/MAO	2.01	90	35.0	oil/152.9	5,097	5.38	nd	nd	nd
43	2 V/MAO	1.00	85	21.0	5.2	173	0.36	nd	nd	nd
24	2 V/MAO	4.16	90	20.0	63.3	2,110	1.77	−68.4	nd	119 000
39	2 V/MAO	4.16	210	21.0	80.2	2,673	2.24	nd	35	303 000
12	1Ti/$Al(iBu)_3/Ph_3CB(C_6F_5)_4$	1.89	80	21.0	3.5	116	0.12	−81.4	nd	nd
27	1Ti/$Al(iBu)_3/Ph_3CB(C_6F_5)_4$	1.73	80	60.0	0	–	–	–	–	nd
31	1Ti/$Al(iBu)_3/Ph_3CB(C_6F_5)_4$	3.30	80	19.0	oil/6.5	217	0.18	nd	nd	nd

Polymerization conditions: toluene (solvent), 2V and 1Ti: 0.03 mmol, MAO: 3 mmol, $Al(iBu)_3/Ph_3CB(C_6F_5)_4$: 0.45/0.06 mmol. [a] 2V: 0.015 mmol.
[b] *C* conversion. *nd* not determined

Table 2 Results of 1-octene polymerization with bis(phenoxyimine)complexes

Entry	Catalyst	Monomer [mol/dm³]	Time [min]	T [°C]	Yield [mg]	Productivity [g/mol$_M$]	C[a] [%]	T_g [°C]	[mmmm] [%]	M$_w$ [g/mol]
17	6 V/MAO	1.9	60	0.5	20.8	693	0.73	−67.7	70	nd
34	6 V/MAO	1.9	60	35	17.3	577	0.61	nd	nd	nd
20	6 V/MAO	1.9	220	22.9	82.5	2,750	2.89	−65.5	nd	435 000
45	6 V/MAO	3.77	210	19.0	149.5	4,983	4.18	−69.3	42	nd
46	6 V/MAO	3.77	60	19.0	67.3	2,243	1.88	nd	17	nd
25	6 V/MAO	3.77	90	19.8	121.9	4,063	3.41	−69.5	nd	nd
50	6 V/MAO	3.77	30	19.0	26.6	887	0.74	nd	nd	204 000
44	6 V/MAO	3.77	270	19.0	165.1	5,503	4.62	nd	nd	576 000
30	7 V/MAO	3.64	90	19.8	oil[b]	–	–	–	–	nd
26	8 V/MAO	3.90	90	19.8	16.5	550	0.46	nd	nd	nd
48	9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$	1.56	120	19.0	55.5	1,850	1.94	−76.8	56	nd
68	9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$	2.73	120	24.5	111.5	3,717	3.12	−76.8	nd	259 000
71	9Ti/MAO	3.86	120	24.5	6.6	220	0.19	nd	nd	nd

Polymerization conditions: toluene (solvent), complex: 0.03 mmol, MAO: 3 mmol, Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$: 0.45/0.06 mmol. [a] *C* conversion. [b] very small amount

reaction conducted for 30 and 270 min, respectively) and with broad molecular weight distributions (for some samples the GPC curves were bimodal, Fig. 2, curve 2). The series of bis(phenoxyimine) vanadium complexes (6 V, 7 V, 8 V) exhibited activities which were dependent on the ligand structures. The highest activity of 4,063 g/(mol$_V$·1.5 h) was observed for the complex 6V bearing ligands without *tert*-Bu groups on the phenolate rings. The complexes 7 V and 8 V featuring di-*tert*-Bu phenolates, irrespective of the type of the group bounded to the imine-*N*-atom (naphthyl or phenyl), offered significantly lower activities. One of possible explanations is that the presence of substituents on phenolate rings make coordination and insertion of the 1-octene monomer more difficult due to steric hindrance.
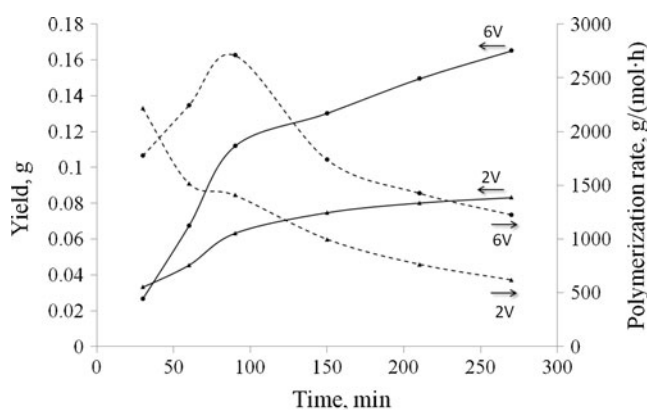
Since *tert*-Bu substituents in phenoxyimine ligands reduce catalytic activity, the 1-octene polymerization process was carried out in the presence of the complex 9Ti. The activity displayed by this complex, when activated by Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$, was moderate but it was significantly higher than that of the titanium complex with salen ligands, and it was dependent on the monomer concentration, which was similar to the performance of other complexes covered by this study (Entry 48 and 68). Moreover, in contrast to the salen complex 1Ti, the complex 9Ti produced polymer after its activation with MAO, although the reaction productivity was very low and the monomer conversion did not exceed 0.2 %.
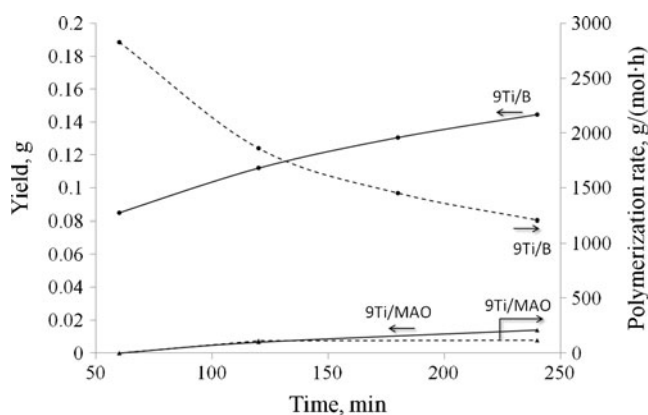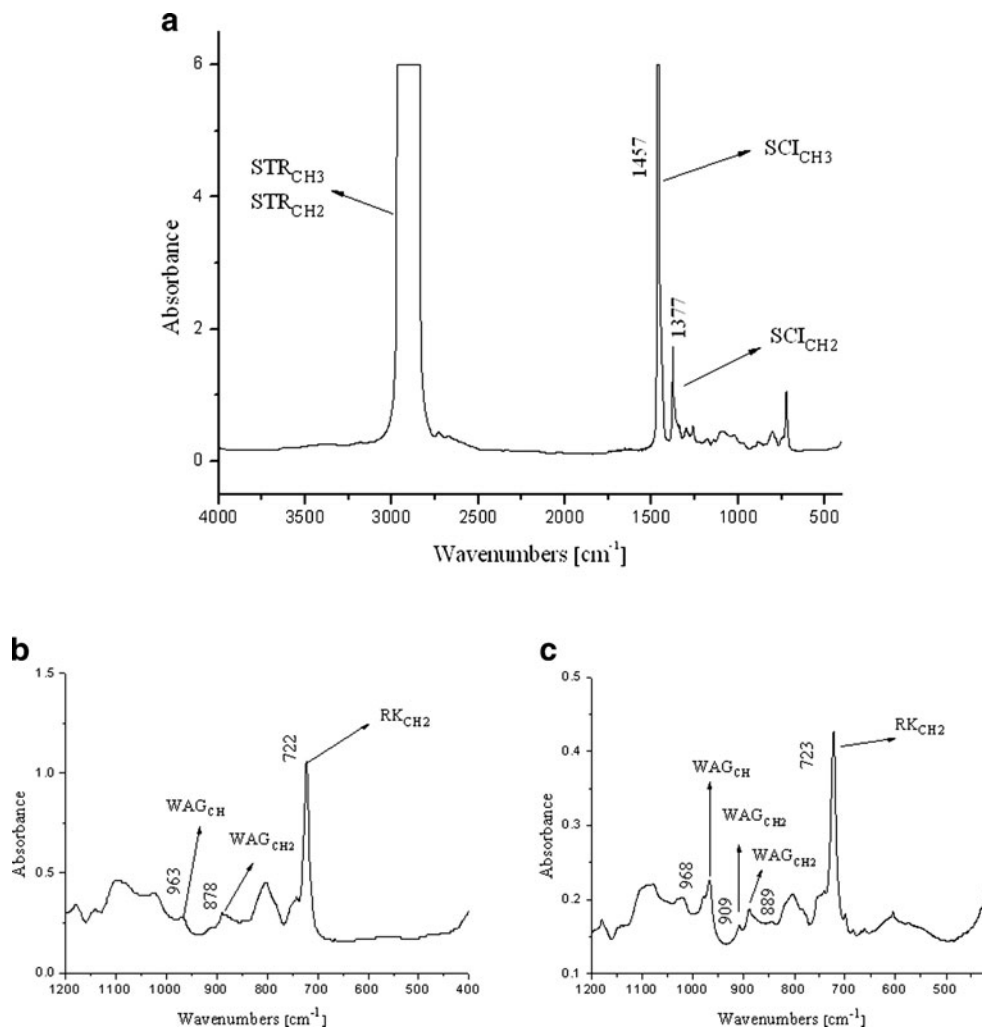

Fig. 3 Effect of polymerization time on poly(1-octene) yield and polymerization rate in reaction catalyzed by catalyst 2V/MAO (*filled triangle*) and catalyst 6V/MAO (*filled circle*). Polymerization conditions: 2V and 6V: 0.03 mmol, MAO: 3 mmol, 1-octene: 4.16 mol/dm³ (polymerization with 2V) and 3.77 mol/dm³ (polymerization with 6V), ambient temperature, toluene (solvent)

Fig. 4 Effect of polymerization time on poly(1-octene) yield and polymerization rate in reaction catalyzed by 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ (*filled circle*) and 9Ti/MAO (*filled triangle*). Polymerization conditions: 9Ti: 0.03 mmol, MAO: 3 mmol, Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$: 0,45/ 0,06 mmol, ambient temperature, 1-octene: 3.20 mol/dm³ (polymerization with 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$) and 3.86 mol/dm³ (polymerization with 9Ti/MAO), toluene (solvent)

Fig. 5 FTIR spectra of poli(1-octene): **a** – spectrum of poli(1-octene) (Entry 17) produced by 6 V/MAO, **b** enlarged section (400–1,200 cm^{-1}) of the sample 17 spectrum, **c** enlarged section (400–1,200 cm^{-1}) of the poly(1-octene) spectrum synthesized with 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ (Entry 67)

The effect of polymerization time on polymer yield and on polymerization rate was studied for selected catalysts. The reaction time was varied from 30 to 270 min. It can be seen from Fig. 3 that the polymerization yield in the process with the use of both vanadium catalytic systems (2 V/MAO and 6 V/MAO) did not increase in proportion to longer reaction times. The polymerization rate for the 2 V/MAO catalyst was highest after 30 min and then it decreased gradually. In case of 6 V/MAO, the polymerization rate increased at the beginning and then, after 90 min, it went down. That decline in the
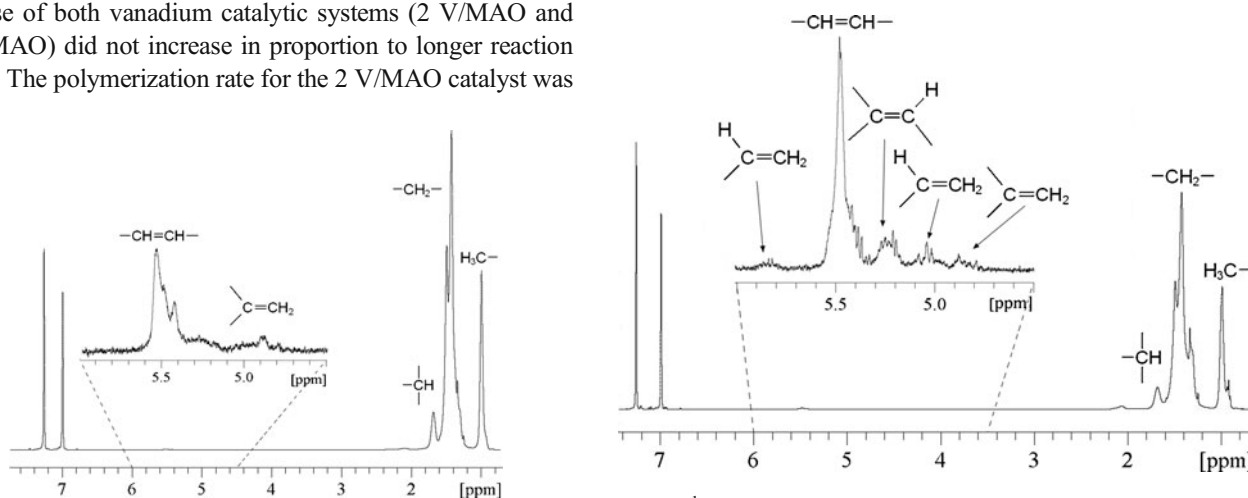

Fig. 6 ^{1}H-NMR spectrum of poli(1-octene) obtained with catalytic system 6 V/MAO (Entry 17) with enlarged olefin region

Fig. 7 ^{1}H-NMR spectrum of poli(1-octene) obtained with catalytic system 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ (Entry 48) with enlarged olefin region
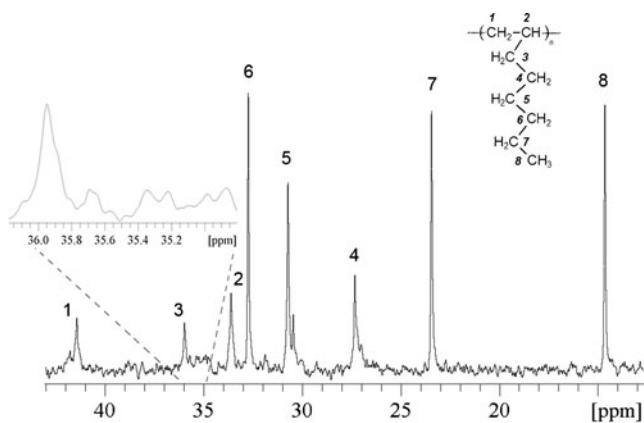
Fig. 8 The ^{13}C NMR spectrum of poly(1-octene) synthesized with 6 V/MAO (Entry 17)

polymerization rate can be caused both by the monomer concentration which decreases and by catalyst deactivation. Having in mind that the maximum monomer conversion obtained in those reactions did not exceed 5 %, it can be concluded that the vanadium active sites are not stable. Indeed, the vanadium catalysts are known for their low stability which is caused by reduction of vanadium to V(II) [17, 18]. And for bis(imino)pyridyne vanadium catalyst was shown that decrease in the catalyst activity with polymerization time results from both the decrease in the active centers number and transformation of some part of initial centers into a new one with lover reactivity [19]. Moreover, taking into account different changes in the polymerization rate over time, one can conclude that phenoxyimine ligands offer better stabilization of the catalytically active species than the salen ones.

The results as presented in Fig. 4 indicate that the polymerization rate for the titanium catalyst 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ also decreases with the reaction time and that the titanium species in 1-octene polymerization are not stable. In case of polymerization with 9Ti/MAO, we observed that the catalyst activity was so
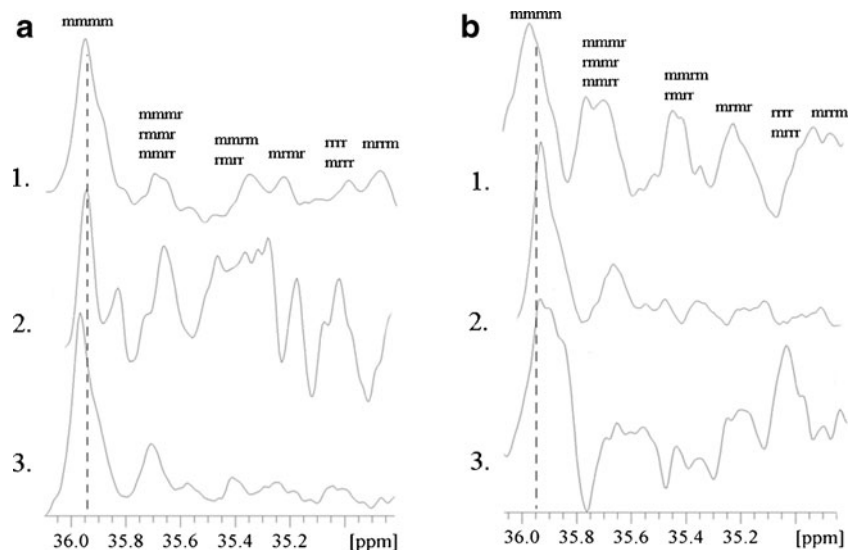
low that no polymer was produced at all after 60 min. Further extension of the polymerization time to 120 and 240 min resulted in the production of poly(1-octene), however its yield was as low as 6.6 and 14 mg, respectively, and those figures correspond to the conversion level of 0.19 % and 0.48 %.

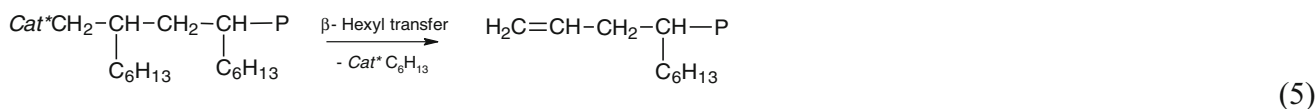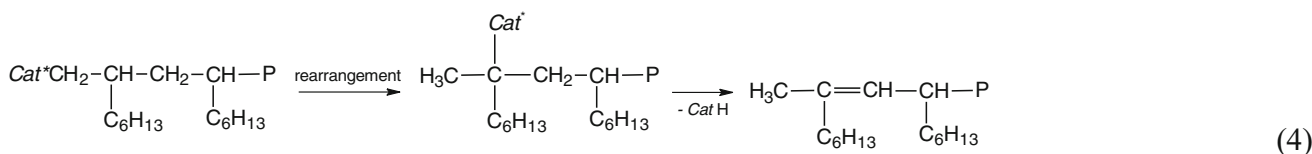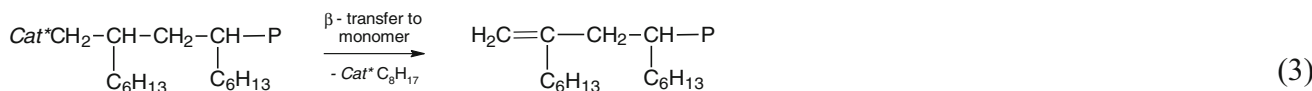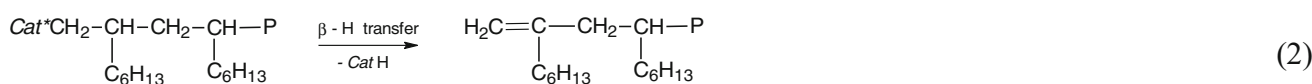### Characterization of poly(1-octene) structure

The polymers obtained in entries: 24, 40 (catalyst 2 V/MAO), 20, 45, 49 (catalyst 6V/MAO), 26 (catalyst 8V/MAO), 67 and 48 (catalyst 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$) were analysed using FTIR spectroscopy. A typical spectrum is presented in Fig. 5a. All spectra involve bands attributable to stretching vibration of C-H (2800–2960 cm^{-1}) and to C-H deformation vibrations in CH$_3$- and CH$_2$- groups (1,457 cm^{-1} and 1,377 cm^{-1}, respectively). In addition, a smaller band at 722 cm^{-1} can be seen which is ascribed to the deformation vibration of methylene groups [RK (CH$_2$)$_n$] in the amorphous phase. In the enlarged part of the spectrum (Fig. 5b), the bands can also be seen which are attributable to C-H out-of-plane deformation vibrations of *trans*-vinylene end groups (around 965 cm^{-1}) and CH$_2$ out-of-plane deformation vibrations of vinylidene end groups (around 880 cm^{-1}). The FTIR spectra of poly(1-octene) produced by titanium complexes possess an additional peak at 909 cm^{-1} which is indicative for the presence of vinyl end-groups. The presence of the mentioned end groups in the vanadium and titanium catalysed poly(1-octene)s was confirmed by the ^{1}H NMR method.

Different proton signals are present in the ^{1}H NMR spectra of poly(1-octenes) synthesized with vanadium complexes 6 V and 2 V (typical spectrum is shown in Fig. 6): the methylene and methine ones between 1.2–1.8 ppm and the methyl one at 0.95 ppm. Moreover, signals for vinylidene end groups (4.8–4.9 ppm) and vinylene end groups (5.35–5.55 ppm) can be seen in the olefinic region. The same signals can be found in

Fig. 9 Expanded C$_3$ region of poly(1-octene)s: a-1) entry 17; a-2) entry 46; a-3) entry 45 in Table 2 and 1-b) entry 1; b-2) entry 39 in Table 1; 3-b) entry 48 in Table 2

the spectra of poly(1-octenes) synthesized with the titanium catalyst. In addition, there are low intensity signals visible at 5.0–5.1 ppm and 5.85 ppm which correspond to the presence of vinyl groups and resonances at 5.2–5.3 ppm in agreement with the presence of tri-substituted unsaturated groups. Figure 7 shows the spectrum of poly(1-octene) obtained in entry 48 as a representative for poly(1-octene)s produced by the titanium catalysts.

Vinylene end groups were dominant in all polymers which indicates that β-hydride elimination after 2,1-inser-

tion of 1-octene was a predominant termination reaction (Eq. 1) [20]. In turn, vinylidene end groups are formed via β-hydride elimination from 1,2-enchained metal alkyl complexes (Eq. 2) or via chain transfer to the monomer (Eq. 3) [2]. Tri-substituted end groups, as present in titanium polymers, can be formed as a result of re-arrangement of the polymer chain which is then terminated by β-H transfer (Eq. 4) [2]. Vinyl end groups, which are also present only in polymers synthesized with titanium complexes, may come from β-alkyl eliminations (Eq. 5) [2].

$$Cat^* \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! CH_2 \!\!-\!\! P \quad \xrightarrow[-\,Cat\,H]{\beta\text{-H transfer}} \quad HC \!\!=\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \tag{1}$$

$$Cat^* CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \quad \xrightarrow[-\,Cat\,H]{\beta\text{-H transfer}} \quad H_2C \!\!=\!\! \underset{\underset{C_6H_{13}}{|}}{C} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \tag{2}$$

$$Cat^* CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \quad \xrightarrow[-\,Cat^*\,C_8H_{17}]{\beta\text{-transfer to monomer}} \quad H_2C \!\!=\!\! \underset{\underset{C_6H_{13}}{|}}{C} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \tag{3}$$

$$Cat^* CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \quad \xrightarrow{\text{rearrangement}} \quad H_3C \!\!-\!\! \underset{\underset{C_6H_{13}}{\overset{\overset{Cat^{\cdot}}{|}}{C}}}{} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \quad \xrightarrow[-\,Cat\,H]{} \quad H_3C \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{C} \!\!=\!\! CH \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \tag{4}$$

$$Cat^* CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \quad \xrightarrow[-\,Cat^*\,C_6H_{13}]{\beta\text{-Hexyl transfer}} \quad H_2C \!\!=\!\! CH \!\!-\!\! CH_2 \!\!-\!\! \underset{\underset{C_6H_{13}}{|}}{CH} \!\!-\!\! P \tag{5}$$

Selected poly(1-octene) samples which were produced by 2 V/MAO, 6 V/MAO and 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ catalytic systems were analysed by ^{13}C NMR spectroscopy to get information about their tacticity. The spectrum of the polymer synthesized with the 6 V/MAO catalytic system (Entry 17) is presented in Fig. 8 as an example. Similar ^{13}C NMR spectra were obtained for all studied poly(1-octene)s, irrespective of the catalytic system used. The sharp and intensive resonance assigned to eight carbon atoms of poly(1-octene) can be seen in the spectra. The observed chemical shifts of C$_1$–C$_8$ carbon atoms (41.41; 33.59; 35.95; 27.32; 30.70; 32.72; 23.42; and 14.64 ppm) are similar to those presented in literature [2, 21].

The signal for C$_3$ carbon atom was used to determine the tacticity on the pentad level. The expanded C$_3$ region of six poly(1-octene)s obtained with different catalytic systems and at different polymerization conditions is shown in Fig. 9. The

assignments of the pentad chemical shifts were based on the data from literature [21] and the ratio of the [$mmmm$] pentad integral to the sum of all pentad integrals was used to calculate the isotacticity degree. The results are shown in Tables 1 and 2.

The highest content of isotactic pentads, i.e. 70 %, was noted for the polymer produced by 6 V/MAO at 0.5 °C (sample 17). The spectra of other poly(1-octene) samples synthesized with bis(phenoxyimine) as well as salen vanadium complexes, which were synthesised at about 20 °C, demonstrated the atactic nature of those polymers since neither [$mmmm$] nor [$rrrr$] sequences were higher than 50 %. It implies a better stereo-control at lower temperatures. A similar effect was observed by Zhao et al. [22] in 1-hexene polymerization with the zirconocene catalyst. Moreover, an increase of isotactic pentad with increasing polymerization time could be seen for vanadium complexes with both phenoxyimine (sample 45 and 46) and

salen (sample 1 and 39) ligands. The titanium catalyst 9Ti/Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$, alike the 6 V/MAO catalyst and the bis(phenoxyimine)Ti complex having a *tert*-butyl substituent in the phenolate ring as described in [23], produces poly(1-octenes) with the atactic structures ([*mmmm*] = 56 %).

Conclusion

1-Octene was polymerized with the use of vanadium and titanium complexes bearing phenoxyimine or salen ligands, upon activation with various co-catalysts. The results obtained indicate that the behaviour of the investigated catalytic systems depended on the type of the metallic centres in the complexes. Vanadium complexes, irrespective of the ligand structure, were active only in conjunction with MAO, whereas titanium complexes required Al(iBu)$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ as an activator. The type of the catalyst affected also the polymerization mechanism. The olefinic end-groups present in the resulting polymers indicate that the main termination reaction for both vanadium and titanium complexes was β-hydride elimination after 2,1-insertion of 1-octene. The contribution of β-hydride elimination from the 1,2-enchained metal alkyl complex or chain transfer to monomer was considerably lower in both reaction systems. And only with titanium complexes the β-alkyl eliminations and rearrangement of polymer chain and then its termination by β-H transfer took place, which lead to vinyl and trisubstituted end groups. All samples investigated by ^{13}C-NMR had atactic structures with [*mmmm*] sequences in the range from 12 to 56 %. The highest amount of isotactic pentad was found for the polymer synthesized at the lowest temperature (70 %).

The type of ligand also affected the catalyst behaviour. In general, complexes with salen ligands are less active then bis(phenoxyimine) complexes and they give products with the lower quantity of [*mmmm*] pentads.

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