

Ethylene/1-olefin copolymerization behaviour of vanadium and titanium complexes bearing salen-type ligand

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Abstract Ethylene/1-olefin copolymerization using vanadium and titanium complexes bearing tetradentate [O,N,N,O]-type ligand and EtAlCl₂ or MAO as a cocatalyst is carried out. In the presence of the vanadium complex activated with EtAlCl₂ is observed (a) negative “comonomer effect”, (b) high comonomer incorporation and narrow chemical composition distribution (CCD), (c) unexpected copolymer microstructure, and (d) increased molecular weight of copolymers when compared with the homopolymer. In contrast, titanium catalyst gives copolymers with lower 1-olefin content and broad CCD. Supported complexes show higher activity, lower 1-olefins incorporation and give copolymers with ultra high molecular weights.

Keywords Copolymerization · Polyolefin · Salen-type complex · Catalysts · Support · Copolymer heterogeneity

Introduction

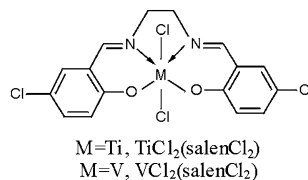
Linear low density polyethylene (LLDPE) synthesised by ethylene/1-olefin copolymerization is a very important commercial product with the global annual production of over 17.2 million tons [1]. Through copolymerization, the structure and properties of polyethylene can be significantly modified and the final properties are dependent principally on the type of the organometallic catalyst employed. Heterogeneous Ziegler–Natta catalysts usually give copolymers with both broad comonomer distribution and wide molecular weight distribution, while

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homogeneous metallocene catalysts produce much more uniform copolymers [2, 3]. Recently copolymerization in the presence of postmetallocene catalysts also became an interesting and important field of research [4–11]. Very efficient copolymerization postmetallocene catalysts are titanium complexes of the general formula $[N-(3,5\text{-di-}i\text{-tert-butylsalicylidene})\text{-}2\text{-alkylsulfanylanilinato}]\text{Ti(IV)Cl}_3$. They are not only highly active but they also give copolymers with high comonomer contents, up to 19.1 mol% [12]. Considerable copolymerization potential is also exhibited by other titanium complexes, and namely those which contain the *o*-carborane-bridged [OSSO]-type tetradentate ligand [13]. Their catalytic activity for ethylene/1-hexene copolymerization is higher than for homopolymerization (positive “comonomer effect”).

The classical vanadium catalysts are known for their ability to produce high molecular weight polyethylene, syndiotactic propylene, and ethylene/1-olefin copolymers with the high 1-olefin content; they are able to perform random and super-random copolymerization [8, 14, 15]. Their specific catalytic properties made them applicable in the production of poly(ethylene-*co*-propylene) and poly(ethylene-*co*-propylene-*co*-diene) elastomers [8, 14, 15]. Hence, much interest was attracted by postmetallocene complexes which had vanadium as the central metal, both for homo- and copolymerization of olefins [5–7, 15–21]. Nomura and Wang [7] used (arylimino)(aryloxo)vanadium(V) complexes in ethylene/1-hexene copolymerization. However, poor 1-hexene incorporation was observed (0.8 mol%). In contrast, vanadium(III) complexes bearing salicylaldiminato ligands produced copolymers with high comonomer incorporation, at certain conditions even at 26.7 mol% of 1-hexene, with high molecular weight and unimodal molecular weight distribution [6]. Moreover, 1-hexene units in the obtained copolymers were shown to be usually isolated from each other by ethylene units, though block-type sequences were present in a copolymer with a higher comonomer content. Copolymers with similar microstructures and properties, e.g. high molecular weight and unimodal molecular weight distribution, were produced by tridentate Schiff base-chelated vanadium(III) catalysts [16]. The excellent ability to copolymerize ethylene and 1-olefins was offered by the vanadium(III) complexes with the mono (β -enaminoketonato) ligand and two tetrahydrofuran molecules as neutral ligands, and by vanadium(III) complexes with tridentate or tetradentate iminopyrrolyl ligands [5, 15]. These catalysts could produce copolymers with the 1-hexene contents of more than 20 mol%, in which no block type sequences of comonomer were present.

Despite a relatively high interest which is attracted by the use of postmetallocene catalysts in copolymerization of ethylene and higher 1-olefins, no study has so far been reported which would investigate directly the effect of the central metal and the catalyst immobilization on the catalytic activity and the monomer reactivity in the copolymerization reaction. In this paper we thus present the search for of those effects in copolymerization of ethylene and 1-octene with the use of the vanadium and titanium complexes which had salen-type ligands (Scheme 1) and, for comparison, with the use of their supported counterparts. Moreover, we compare the efficiency of the vanadium catalysts, supported and unsupported, in the copolymerization process which involves 1-olefin comonomers with different chain lengths (from 1-hexene to 1-dodecene).

Scheme 1 The structure of complexes

Experimental section

All the operations which involved the catalysts and the activator were performed under the argon atmosphere, with the use of the standard Schlenk and glove box techniques.

Materials

Ethylenebis(5-chlorosalicylideneiminato)vanadium dichloride, $\text{VCl}_2(\text{salenCl}_2)$, and ethylenebis(5-chlorosalicylideneiminato)titanium dichloride, $\text{TiCl}_2(\text{salenCl}_2)$, were synthesised as reported in [22]. The magnesium support, $\text{MgCl}_2(\text{THF})_2/\text{Et}_2\text{AlCl}$, was prepared according to the procedure presented in [23]. Ethylene (3.0 grade, Linde Gas) was used in tests after having been passed through a column packed with sodium metal supported on Al_2O_3 . Solvents were distilled from sodium (toluene) or sodium/benzophenone (hexane) before use. 1-olefins from Aldrich were dried over molecular sieves 4A and 13X. Argon (5.0 grade, Linde Gas), methylaluminoxane (MAO) (10.0 wt%, Aldrich), Et_3Al (25 wt%, Aldrich), Me_3Al (2 M, Aldrich), and EtAlCl_2 (25 wt%, Aldrich) were used without further purification. The supported catalysts Sup-V and Sup-Ti were obtained by ball-milling of the magnesium carrier, $\text{MgCl}_2(\text{THF})_2/\text{Et}_2\text{AlCl}$, and the salen complex of vanadium ($\text{VCl}_2(\text{salenCl}_2)$) or titanium ($\text{TiCl}_2(\text{salenCl}_2)$). Synthesis was performed according to the procedure reported previously [23, 24].

Copolymerization

Ethylene/1-olefin copolymerization was carried out in a Büchi glass autoclave equipped with the stirrer and heating-cooling jacket. Under typical copolymerization conditions, toluene or hexane (solvent, 150 ml), 1-olefin and the required amount of activator were mixed in the autoclave under argon blanketing, and then the appropriate volume of the complex solution in toluene or the suspension of the supported catalyst in hexane was added. Finally, ethylene was introduced. The ethylene feed pressure (5 atm.) and the reactor temperature were kept constant throughout the runs. The reaction was carried out for 0.5 h (unless mentioned otherwise) and then it was quenched by adding a dilute solution of hydrochloric acid in methanol. The obtained polymer was filtered, washed a few times with methanol and dried in vacuo. The ethylene homopolymerization followed the same procedure and the only difference was that no 1-olefin was charged to the reactor.

Characterization of copolymers

FT-IR spectra were recorded using Nicole Nexus, 2002 FT-IR spectrometer. Copolymers were pressed into disc with KBr and scans were taken in the range from 4,000 to 400 cm^{-1} with a 2 cm^{-1} resolution. The ATR scanning technique was used for sample materials from which it was hard to form tablets. The compositions of copolymers were determined using the A_{1379}/A_{1368} absorbance ratios obtained by separation of analytical bands [25]. Vinyl, *trans*-vinylene, vinylidene, and trisubstituted vinylenes end groups relative contents were estimated from the peak intensities at 992, 909, 965, 888, and 840–790 cm^{-1} , respectively, which were normalized using the peak at 2,020 cm^{-1} , which is proportional to the sample thickness. The ^{13}C -NMR spectra of the copolymers were recorded on Ultrashield Bruker 400 MHz spectrometer in 1,2-dichlorobenzene- d_4 at 120 °C. The numbers of scan performed for each spectrum was at least 8000. The chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken to be 30.00 ppm. The average molecular weights (M_w) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography using the Alliance 135 GPCV 2000 apparatus equipped with columns: HT3, HT4, and HT6E. The measurements were performed at 135 °C, with 1,2,4-trichlorobenzene as the solvent, and at the flow rate of 1.0 ml/min. The narrow molecular weight distribution polystyrene standards were used for calibration. DSC analyses were carried out with the use of the 2010 DSC calorimeter from TA Instruments. The heat of fusion (ΔH_f) and melting point (T_m) data were measured for samples which had been previously melted and recrystallized at the heating rate of 10 K/min. Based on ΔH_f , percentage of crystallinity was calculated as $X_c = \Delta H_f \times (100/290)$ [26]. The SSA fractionation was performed with the use of the same apparatus and according to the principles described earlier [27].

Results and discussion

Ethylene/1-olefin copolymerization behaviour of vanadium complex

The vanadium complex (Scheme 1) was investigated for ethylene/1-octene copolymerization in the presence of the co-catalyst (EtAlCl_2) and at the polymerization conditions applied earlier for ethylene homopolymerization [22]. The obtained results were summarized in Table 1. The catalytic activity of this complex was medium and it was clearly dependent on the comonomer concentration in the feed. It should be noted that the presence of a comonomer and its concentration in the polymerization feed always affect the catalytic activity; that is called a “comonomer effect”. The comonomer, however, may affect the reaction in different ways—depending on the polymerization conditions and on the type of the catalyst [28]. In that specific case we observed the negative “comonomer effect”, i.e. the use of the comonomer and its increasing concentration led to lower activity: from 1,217 kg/(mol V 0.5 h) for homopolymerization down to 461 kg/(mol V 0.5 h) for copolymerization conducted at the highest 1-octene concentration, 1.340 mol/l. The similar relation for the

Table 1 Copolymerization results of ethylene with 1-octene by the $VCl_2(\text{salen}Cl_2)/EtAlCl_2$ catalyst system

Run no.	Time (min)	1-Octene (mol/l) ^a	Yield (g)	Activity ^b	1-Octene content (mol%)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	T_m (°C)	χ (%)
1,118	30	–	8.52	1,217	–	523	4.5	136.3	57.3
9	30	0.104	7.84	1,120	0.7	–	–	136.6	56.6
7	30	0.206	6.81	973	1.1	343	6.7	137.8	53.2
8	30	0.398	4.83	690	3.6	374	6.7	135.7	56.4
10	30	0.579	4.22	603	5.5	392	6.7	134.1	50.9
11	30	0.749	3.91	559	7.7	554	6.3	133.1	57.8
12	30	1.060	3.78	540	11.8	899	5.5	130.5	39.8
15	30	1.340	3.23	461	15.2	1,261	6.9	132.2	30.0
17	10	0.398	3.11	1,332	5.5	–	–	135.8	57.7
16	40	0.398	5.45	584	3.7	–	–	136.1	50.0
13	60	0.398	6.38	456	3.7	–	–	135.3	62.0

Copolymerization conditions: complex 0.007 mmol, $EtAlCl_2$ 3.6 mmol, $Al/V = 514$ (mol/mol), 30 °C, ethylene 5 atm., toluene 150 ml

^a 1-octene concentration in the feed

^b Activity in kg of polymer/(mol V 0.5 h)

– Not determined

catalytic activity versus comonomer concentration was also observed for other comonomers: 1-hexene and 1-decene (Table 2).

At the same time, the amount of 1-octene and other comonomers initially added to the polymerization feed affected the 1-olefin content in the polymer. As expected, the increase of comonomer concentrations led to higher incorporation. Thus, incorporation of 1-octene at concentration of 0.104 mol/l amounted to about 0.7 mol%, while at the highest concentration of comonomer, i.e. 1.340 mol/l, incorporation reached as high level as about 15.2 mol% (Table 1). Similar incorporation of 1-decene into the copolymer (15.9 mol%) was obtained at the 1-decene concentration in the reaction medium of 1.112 mol/l. The highest incorporation of 1-hexene was only 8.2 mol% (Table 2) despite the fact that the monomer concentration was highest, 1.696 mol/l. Thus, the olefin with the shortest carbon chain offered the lowest incorporation efficiency. The opposite relation is usually observed, i.e. long chain 1-olefins have lower incorporation levels into polyethylene chains due to lower coordination ability of bulkier 1-olefins [29–31].

Although the comonomer incorporation level observed was high, yet it was lower than the one available for other vanadium-based catalysts [5, 6]. It seems that the efficiency of comonomer incorporation by the studied catalyst was in principle limited by the adopted reaction conditions, i.e. relatively high pressure of ethylene (5 atm.) and longer reaction time (30 min), instead of 1 atm. and 10 min as reported in the quoted papers. Indeed, the amount of comonomer in copolymer decreased for longer reaction times, with other polymerization conditions kept constant

Table 2 Copolymerization results of ethylene with 1-decene and 1-hexene by the $VCl_2(\text{salen}Cl_2)/EtAlCl_2$ catalyst system

Run no.	1-Olefin (ml)	1-Olefin (mol/l) ^a	Yield (g)	Activity ^b	1-Olefin content (mol%)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	T_m (°C)	χ (%)
50	2.5 Dec	0.087	3.74	534.3	1.4	368	7.2	136.4	58.2
51	10.0 Dec	0.330	3.55	507.1	5.0	423	6.1	135.5	55.1
52	20.0 Dec	0.621	3.31	472.9	8.8	699	5.1	131.2	41.0
53	40.0 Dec	1.112	2.45	350.0	15.9	1,473	7.2	124.6	21.3
59	10.0 Hex	0.503	4.28	611.4	1.3	–	–	136.5	53.0
60	20.0 Hex	0.948	3.53	504.3	3.9	–	–	136.2	54.5
61	40.0 Hex	1.696	3.10	442.9	8.2	–	–	134.3	49.6

Copolymerization conditions: complex 0.007 mmol, $EtAlCl_2$ 3.6 mmol, $Al/V = 514$ (mol/mol), 30 °C, 30 min, ethylene 5 atm., toluene 150 ml

^a 1-Olefin concentration in the feed

^b Activity in kg of polymer/(mol V 0.5 h)

Dec 1-decene, *Hex* 1-hexene, – Not determined

(Table 1, runs 13, 14, 16, 17, 8). Comonomer content in the polymer was equal 5.5 mol% after 10 min and dropped down to about 3.7 mol% if the reaction was continued over 1 h. The obtained results showed also that the copolymer yield increased for the increasing polymerization time, but the catalyst activity reached its peak value, 1,332 kg/(mol V 0.5 h), at the shortest polymerization time (run 17) and then it gradually decreased for longer reaction times. The loss of activity over time is, however, a common trend for vanadium catalysts [14].

Introduction of a comonomer and increasing its concentration affected the polymer melting point and its crystallinity. Both the melting point and heat of fusion (ΔH_f), on the basis of which the percentage of crystallinity is calculated, are known to be dependent on the density of comonomer (branch density) and they decline for increasing density values [32]. So, decrease was observed in polymer crystallinity from 57.3 % for the homopolymer to 30 % for the copolymer with higher 1-octene content (Table 1, run 1118 and 15, respectively). Similarly, the melting point of the copolymer declined for higher concentrations of 1-octene. The same clear trends were also observed for ethylene/1-hexene and ethylene/1-decene copolymers (Table 2).

The comonomer concentration affected the molecular weight of the obtained copolymers as well. M_w went down initially for the increasing concentration of 1-octene, from 523,000 g/mol (M_w of homopolymer) to 343,000 g/mol (0.206 mol/l of 1-octene). Any further increase in the comonomer concentration produced higher M_w values up to 1,261,000 g/mol (Table 1, run 15). The situation was similar for copolymerization with 1-decene. The molecular weight of the copolymer product declined initially for growing concentrations of 1-decene, down to 368,000 g/mol, and then it climbed up to 1,473,000 g/mol (Table 2, runs 50 and 53, respectively). Such behaviour of catalyst is not typical for ethylene/1-olefin copolymerization.

Usually, decline in molecular weights versus increasing comonomer concentrations is observed for different catalyst types which may be attributed to elimination of β -hydride [5, 11, 29].

The obtained ethylene/1-octene copolymers possessed the moderate values of M_w/M_n . Moreover, M_w/M_n values were independent on the amount of 1-octene in the copolymerization feed in practice, and they fell within 5.54–6.95. Therefore active sites in that system showed similar reactivity towards the comonomer. Similar values of M_w/M_n and very small changes in those values versus composition could be noted for ethylene/1-decene copolymers (Table 2, runs 50–53). That behaviour, e.g. independence of molecular weight distribution on the comonomer concentration, is usually observed for single-site catalysts [11].

Ethylene/1-octene copolymerization behaviour of titanium complex

Copolymerization of ethylene with 1-octene was also studied in the presence of the titanium complex (Scheme 1). Copolymerization conditions and the cocatalyst type were selected on the basis of our previous ethylene polymerization study [33]. Thus, copolymerization tests were conducted with MAO as the co-catalyst, in toluene, at 50 °C, for 30 min. The results are presented in Table 3. As can be seen, the catalytic behaviour of the titanium catalyst is different than that of the vanadium one. With the increase of 1-octene in the feed, the catalytic activity of the titanium complex towards copolymerization hardly changes initially with changing comonomer concentrations and the negative “comonomer effect” can be observed at the highest comonomer contents only.

The data on the comonomer content in the copolymer versus comonomer concentration in the feed are also given in Table 3. And again, the more 1-octene was added initially, the more of it was incorporated into the polymer chain. However, the titanium complex incorporated significantly less 1-octene than its vanadium counterpart. At the highest comonomer concentration, 1.340 mol/l, the copolymer containing 5.5 mol% of 1-octene was obtained while (for the same comonomer concentration) the vanadium complex produced the copolymer having 15.2 % of comonomer. This is in line with the study on the supported classical vanadium and titanium Ziegler–Natta catalysts [34].

The GPC analyses revealed high molecular weights for the copolymers produced by the titanium complex, over one million g/mol, and those values were even higher than those for the copolymers synthesized with the vanadium complex. Moreover, molecular weight distributions of the titanium polymers were very broad and much wider than those of the vanadium ones. The changes in molecular weights of titanium copolymers for changing comonomer concentrations in the reaction medium were relatively small, while the comonomer concentration strongly affected M_w/M_n values of the products. In case of polyethylene, M_w/M_n was about 30, and the introduction of 1-octene resulted in considerable broadening of M_w/M_n , up to about 155 for copolymers which had been produced at the comonomer concentration of 1.340 mol/l (Table 3; Fig. 1). Moreover, the GPC profiles for polyethylene (run 1121) and copolymer obtain in run 20 showed long tails within lower molecular weights (curves 1 and 2), whereas the chromatograms of copolymers obtained at higher comonomer

Table 3 Copolymerization results of ethylene with 1-octene by the $\text{TiCl}_2(\text{salenCl}_2)/\text{MAO}$ catalyst system

Run no.	1-Octene (mol/l) ^a	Yield (g)	Activity ^b	1-Octene content (mol%)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	T_m (°C)	χ (%)
1,121	–	1.27	18.1	–	1,366	30.7	137.6	56.7
19	0.104	1.54	22.0	2.2	1,023	49.3	128.8	49.1
20	0.206	1.52	21.7	2.3	1,311	44.8	126.1	42.4
21	0.398	1.45	20.7	3.2 ^c	1,209	57.1	126.3	38.3
22	0.579	1.35	19.3	–	1,077	81.3	123.1	35.0
23	0.749	1.28	18.3	4.7 ^c	1,136	144.5	122.1	31.1
24	1.060	1.14	16.3	–	–	–	–	–
25	1.340	1.03	14.7	5.5 ^c	1,577	154.5	100.7; 118.8	–

Copolymerization conditions: complex 0.07 mmol, MAO 10.5 mmol, Al/Ti = 150 (mol/mol), 50 °C, ethylene 5 atm., 30 min, toluene 150 ml

^a 1-Octene concentration in the feed

^b Activity in kg of polymer/(mol Ti 0.5 h)

^c Determined by ATR method

– Not determined

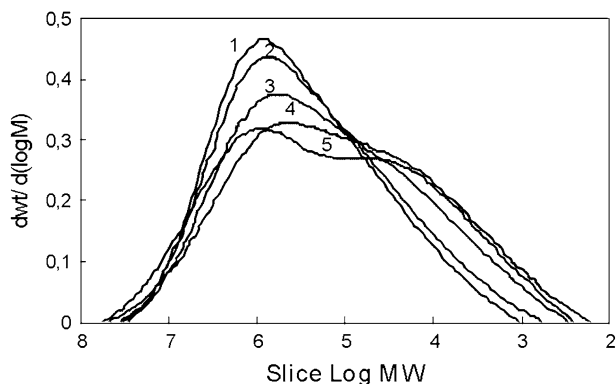


Fig. 1 Gel permeation chromatograms of polyethylene and ethylene/1-octene copolymers produced by $\text{TiCl}_2(\text{salenCl}_2)/\text{MAO}$ 1 run 1121, 2 run 20, 3 run 22, 4 run 23, 5 run 25 in Table 3

concentrations (Fig. 1, curves 3–5) showed shoulder peaks or even bimodal shapes. That broad distributions of molecular weights had been also observed earlier for other titanium catalysts with multichelated ligands [35].

So large values of M_w/M_n copolymers produced by the titanium catalyst, can be indicative not only for the formation of many active species but also for the change of their nature in the course of the polymerization process. Brabanov et al. [36] showed for the iron catalyst that highly reactive but unstable active sites were dominant initially in the reaction, and that they yielded low molecular weight products. But at the later polymerization stage(s), polyethylene with higher M_w was

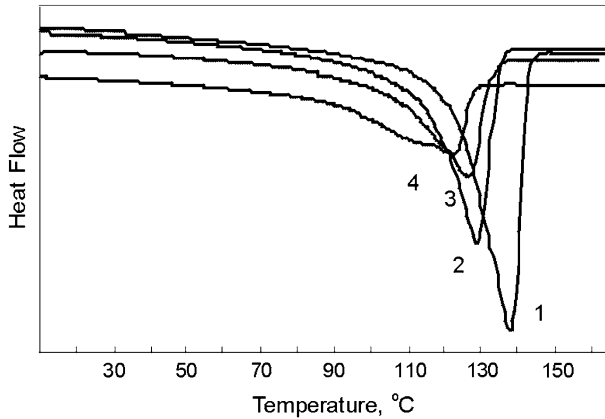


Fig. 2 DSC thermograms of polyethylene and ethylene/1-octene copolymers produced by $\text{TiCl}_2(\text{salenCl}_2)/\text{MAO}$ catalyst 1 run 1121, 2 run 19, 3 run 21, 4 run 23 in Table 3

produced by less active but more stable active sites. Moreover, the comonomer concentration in copolymerization in the presence of titanium catalyst, in contrast to copolymerization with vanadium one, have a great impact on copolymers polydispersity. Higher concentrations resulted in significant broadening of the molecular weight distribution which might come from the fact that different sites incorporated the comonomer with different efficiencies. One might suppose, moreover, that—as with Ziegler–Natta systems—the catalytic active sites which produced macromolecules with shorter chains had also the tendency to incorporate more comonomer and the longer chains were more linear [37].

The DSC thermograms of polyethylene and ethylene/1-octene copolymers obtained at different comonomer concentrations are presented in Fig. 2. As can be seen, the melting points of those copolymers decreased with the increase of the 1-octene content in the polymer. Moreover, the shape of endothermic peaks was dependent on the polymer composition. Comonomer incorporation led to broadening of peaks and even two melting peaks could be observed. Such shapes of DSC curves could be indicative of the presence of the polymer fractions with different comonomer content.

Effect of comonomer concentration and catalyst type on heterogeneity of copolymers

To investigate the effect of the comonomer content and catalyst type on the copolymer chemical composition distribution (CCD), successive self-nucleation/annealing (SSA) analyses were carried out. This method is based on the sequence of self-nucleation and annealing steps to a polymer sample and has been recognized as a useful tool to qualitatively characterize the comonomer distribution in ethylene/1-olefin copolymers [38, 39]. In this work we selected three samples of ethylene/1-octene copolymers produced by the titanium complex (comonomer content: 3.2, 4.7, and 5.5 mol%), and two copolymers synthesized with the vanadium catalyst

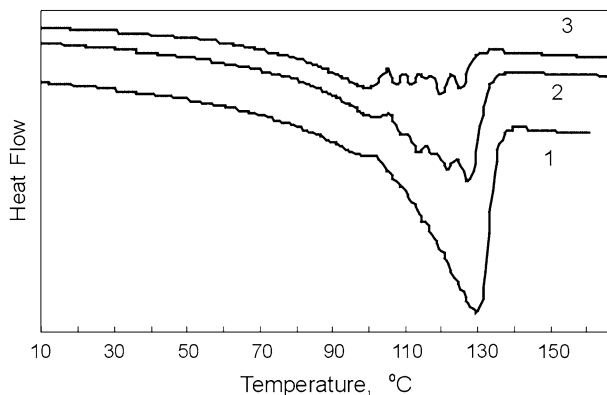


Fig. 3 DSC thermograms of ethylene/1-octene copolymers made by $\text{TiCl}_2(\text{salenCl}_2)/\text{MAO}$ catalyst after SSA thermal treatment 1 run 21, 2 run 23, and 3 run 25 in Table 3

containing 3.6 and 15.2 mol% of the comonomer. The DSC thermograms after the SSA thermal treatment are shown in Figs. 3 and 4, respectively. As can be seen, the SSA profiles of copolymers obtained with $\text{TiCl}_2(\text{salenCl}_2)/\text{MAO}$ are quite different for various comonomer content. Those differences indicate that the increasing comonomer content in copolymers have broadening effect on their CCD. The melting range of the copolymer having the lowest comonomer content after SSA treatment was broad and it extended down to about 30 °C from its peak value at 129° (Fig. 3, curve 1). So, we could suppose that melting of individual fractions occurred within such a narrow temperature interval that they did not separate into different peaks. Increased comonomer content to 4.7 mol% (Fig. 3, curve 2, copolymer obtained in run 23) made melting peaks clearly outlined in the DSC curve with the melting points in the range 126.8, 121.2, 117.3, 113.3, 108.6, and 101.7 °C. In turn, the SSA profile of copolymer obtained in run 25, with the highest comonomer content, showed six distinct melting endotherms (Fig. 3, curve 3) the distribution of which is clearly bimodal. That may be assumed to reflect the bimodal distribution of the short chain branching in the copolymer. The increase in the comonomer content from 4.7 to 5.5 mol% did not give any additional peaks but it caused a shift in the ranges of melting points from 126.8–101.7 to 124.7–99.35 °C.

The analysed copolymers were characterised by very wide distributions of their molecular weights and that technique is theoretically also capable of fractionating linear chains of different molecular lengths. However, the SSA parameters were selected in such a way that the chains underwent fractionation according to the size of their crystallisable sequences and the molecular weight distribution by fractionation was limited [39]. So, in order to check the substantial effect of very broad molecular weight distribution on DSC thermograms after SSA procedure, the SSA method was utilised to fractionate the ethylene homopolymer with $M_w/M_n = 30.7$ (Table 3, run 1121) and the thermogram with one narrow melting peak at 139.2 was obtained.

The DSC scan of ethylene/1-octene copolymers produced by $\text{VCl}_2(\text{salenCl}_2)/\text{Et}_2\text{AlCl}$ (Fig. 4), irrespective of comonomer incorporation (run 8 and 15, Table 1),

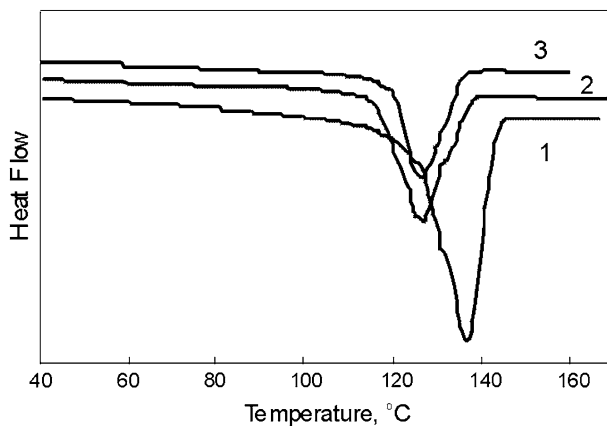


Fig. 4 DSC thermograms of ethylene/1-octene and ethylene-1-decene copolymers made by $VCl_2(\text{salen}Cl_2)/EtAlCl_2$ catalyst after SSA thermal treatment 1 run 8 and 2 run 15 in Table 1, 3 run 53 in Table 2

after SSA treatment showed only one melting peak the location of which was dependent on the amount of incorporated comonomer—136.6 and 130.3 °C for the copolymers with lower (run 8) and higher (run 15) 1-octene units. Nevertheless, some imperfection in the chain composition was apparent in case of copolymer obtained in run 15—the melting peak was somewhat irregular in its shape. It must be stressed that even metallocene catalysts which are considered single-site produce copolymers for which, after SSA fractionation, thermograms are obtained which contain several melting peaks [40]. To confirm those unexpected results, the SSA procedure was applied also for ethylene/1-decene copolymer with the highest comonomer content and produced by the vanadium catalyst (run 53, Table 2). The obtained thermogram, curve 3 presented in Fig. 4, entirely proved the previous results. Hence, the copolymers synthesized with the vanadium catalyst are uniform from the viewpoint of their chemical compositions. As far as we know, there are previous examples of copolymers with such homogeneous comonomer chain distributions.

Copolymer structure characterization

Unsaturated end group analysis was carried out on poly(ethylene-*co*-1-octene) samples with different 1-octene content produced with $VCl_2(\text{salen}Cl_2)/EtAlCl_2$ (Table 1, run 8, 11, and 15) and $TiCl_2(\text{salen}Cl_2)/MAO$ (Table 3, run 19, 20). The exemplary spectra are presented in Fig. 5 and as can be seen various unsaturated end groups are present in the copolymers. The different unsaturation type is formed as the result of different termination reactions during copolymerization. The most relevant termination reaction during copolymerization was described before [5, 41, 42]. In copolymer produced by titanium catalysts the vinyl end groups are main. Formation of vinyl group is connected with β -hydrogen elimination or β -hydrogen transfer to the monomer with the ethylene as the last inserted monomer. Vinylidene

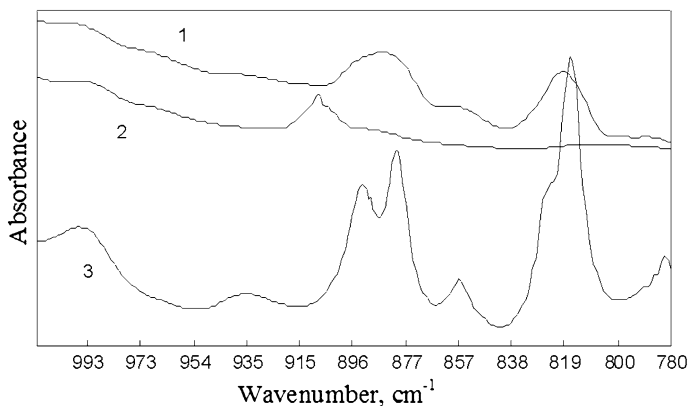


Fig. 5 The vinyl region in the FTIR spectra of the poly(ethylene-*co*-1-octene)s obtained with vanadium and titanium catalysts 1 run 15, 2 run 20 and poly(ethylene-*co*-1-decene), 3 run 53

unsaturation, which are coming from β -hydrogen elimination or β -hydrogen transfer to the monomer with 1-octene as a last inserted monomer after 1,2 insertion, are dominant in copolymers synthesised with vanadium catalyst. In addition, in the spectra of copolymers produced with vanadium catalysts the peak at 820 cm^{-1} with high intensity was observed what can indicate the presence of trisubstituted end groups (the absorption range $840\text{--}790\text{ cm}^{-1}$) [42]. Such end groups are formed when the higher olefin is the last inserted monomer and isomerization and β -H transfer to the metal center occurs [42]. The spectra of titanium copolymers also contain peak in the absorption range for trisubstituted alkene, though its maximum is at about $804\text{--}809\text{ cm}^{-1}$. It should be added that in both vanadium and titanium copolymers amount of *trans*-vinylene was extremely low what indicate that the termination after 2,1-insertion of comonomer is not significant. The ethylene/1-decene copolymers made by vanadium catalyst similarly to ethylene/1-octene vanadium copolymers have trisubstituted vinylene and vinylidene as major unsaturation and do not contain any the *trans*-vinylene groups. Moreover, the FTIR spectrum of copolymer with the highest 1-decene content (run 53) indicates presence of two different vinylidene groups (peaks at 880 and 892 cm^{-1}) (Fig. 5, run 53).

The selected copolymers were analyzed with ^{13}C NMR spectroscopy. The carbon and sequence assignments for ethylene-1-octene copolymers was made according to [43]. The spectrum of poly(ethylene-*co*-1-octene) copolymer containing about 5.5 mol% of 1-octene units produced by titanium catalyst at highest comonomer concentration in the feed (1,340 mol/l) is presented in Fig. 6. This spectrum is similar to those presented in other works for copolymers with not very high comonomer content [29, 44] and exhibits signals, which can be attributed to CH_3 (14.04 ppm, EOE + OOE + EOO + OOO), $\text{CH}_2(2)$ (22.88 ppm, EOE + OOE + EOO + OOO), $\text{CH}_2(5)$ (27.28 ppm, EOE), $\beta\delta$ (27.34 ppm, OEE + EEO), $\delta\delta + \text{CH}_2(4)$ (30.00 ppm, EEE + EOE + EOO + OOE + OOO), $\gamma\delta$ (30.51 ppm, OEEE + EEEO), $\text{CH}_2(3)$ (32.21 ppm, EOE + OOE + EOO + OOO), $\alpha\delta + \text{CH}_2(6)$ (34.61 ppm, EOEE + EEOE + EOE), and CH (38.25 ppm, EOE).

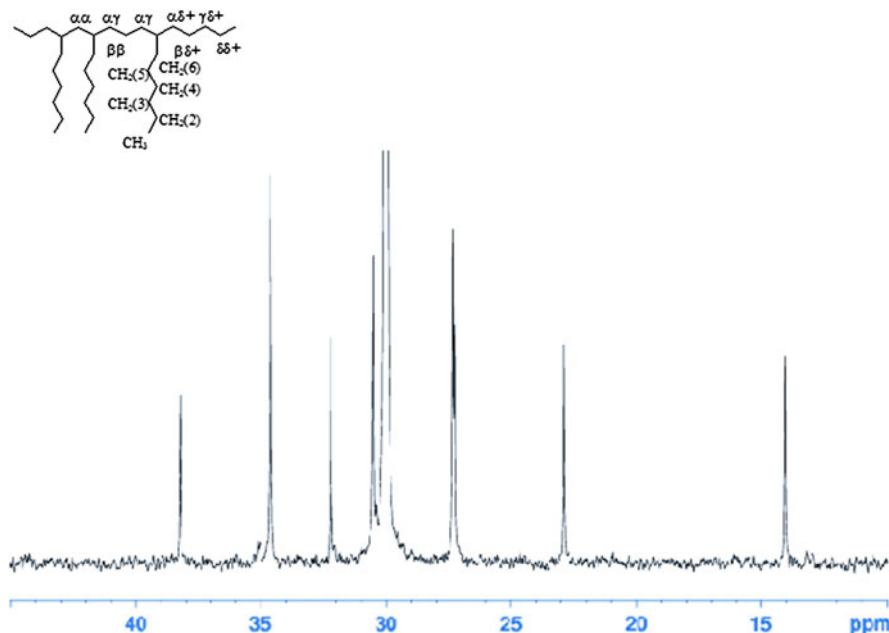


Fig. 6 ^{13}C NMR spectrum of poly(ethylene-*co*-1-octene) obtained using $\text{TiCl}_2(\text{salenCl}_2)/\text{MAO}$ catalyst (run 25)

The spectra of poly(ethylene-*co*-1-octene)s and poly(ethylene-*co*-1-decene)s synthesized with vanadium catalyst turned out to be quite different from typical spectra of ethylene/1-olefin copolymers known from literature and the signal assignment and the copolymerization mechanism in the presence of vanadium catalyst needs further detail examination.

Ethylene/1-olefin copolymerization behaviour of supported catalysts

Homogeneous postmetallocene catalysts, similar to metallocene catalysts, may potentially be employed in industrial processes after immobilization on a carrier only. Our previous study revealed that immobilization of both vanadium and titanium salen-type complexes on the magnesium support of the formula $\text{MgCl}_2(\text{THF})_{0.32}(\text{Et}_2\text{AlCl})_{0.36}$ gave highly effective catalysts for ethylene polymerization [23, 24]. In this work, we check whether immobilization of salen complexes changed their copolymerization ability. As cocatalyst MAO and trialkylaluminium were used because only those compounds could effectively activate supported catalysts. As can be seen in Table 4, the activity of both vanadium and titanium supported catalysts was significantly higher than their nonsupported counterparts and for both catalysts negative “comonomer effect” was observed. Alike for polyethylene, ethylene/1-octene copolymers synthesised with Sup-V possessed clearly higher molecular weights than copolymers produced by the complex $\text{VCl}_2(\text{salenCl}_2)$ at the same comonomer concentration. Moreover, their M_w/M_n values

Table 4 Copolymerization results of ethylene with 1-octene by the Sup-V and Sup-Ti catalyst activated by MAO

Run no.	Catalyst	1-Octene (mol/l) ^a	Yield (g)	Activity ^b	1-Octene content (mol%)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	T_m (°C)	χ (%)
1,122	Sup-V	–	26.80	957.1	–	3,975	42.6	135.1	46.2
26	Sup-V	0.104	24.16	862.9	0	–	–	130.2	43.1
27	Sup-V	0.206	23.44	837.1	0.5	3 192	70.6	128.1	41.0
28	Sup-V	0.398	21.83	779.6	0.65	3 871	47.3	128.1	41.0
29	Sup-V	0.579	20.42	729.3	0.6	2 869	50.5	127.5	42.2
32	Sup-V	1.340	5.4	192.9	0.7	2 362	35.1	127.4	40.7
55	Sup-V ^c	0.398	7.98	285.0	0.2	–	–	129.3	41.8
56	Sup-V ^c	0.749	7.55	269.6	0.2	–	–	128.2	43.8
57	Sup-V ^c	1.340	4.76	170.0	0.6	–	–	127.2	42.4
1,125	Sup-Ti	–	27.24	389.1	–	–	–	137.3	52.3
63	Sup-Ti	0.104	25.9	370.0	0.4	–	–	130.6	47.1
64	Sup-Ti	0.398	24.13	344.7	0.5	–	–	128.1	52.5
65	Sup-Ti	0.749	21.83	311.9	0.8	–	–	129.4	41.0
66	Sup-Ti	1.340	19.38	276.9	0.9	–	–	130.3	46.6

Copolymerization conditions: Sup-V 0.028 g, Sup-Ti 0.07 g, activator 8 mmol, Al/V = 2312, Al/Ti = 494, 30 min, ethylene 5 atm., hexane 150 ml, polymerization temp. 30 °C for vanadium and 50 °C for titanium catalyst

^a 1-Octene concentration in the feed

^b Activity in g of polymer/(g cat 0.5 h)

^c Activator Me₃Al

– Not determined

were very broad and a few times higher than M_w/M_n of copolymers produced by nonsupported catalyst (29.1–70.6 vs. 5.5–6.9) (Table 4; Fig. 7).

In addition, the presence of 1-octene and its concentration in the feed impacted the melting points of copolymers produced by both supported catalysts (Table 4). It decreased with the increase of the comonomer concentration, although the changes were not so distinct as in the case of copolymers synthesized with nonsupported catalysts. For example, melting point of PE and copolymer produced at the highest comonomer concentrations (1.340 mol/l) by Sup-V/MAO were found as: 135.1 and 127.4 °C, respectively. Similarly, the changes in crystallinity of copolymers obtained from supported catalysts covered a lower span than changes in crystallinity of copolymers produced by unsupported ones. That relatively small change in the properties could indicate that the comonomer incorporation to the polyethylene chain was rather small. Indeed, irrespective of the composition of the employed catalytic system the 1-octene content in those copolymers don't exceeded 1 mol%. Thus, the support played the role of a huge ligand which markedly changed accessibility of the active site for the comonomer molecules. The comonomer incorporation was also definitely lower than for the classical supported Ziegler–Natta catalysts. VCl₄/MgCl₂(THF)₂/Et₂AlCl catalytic system, at 0.653 mol/l of

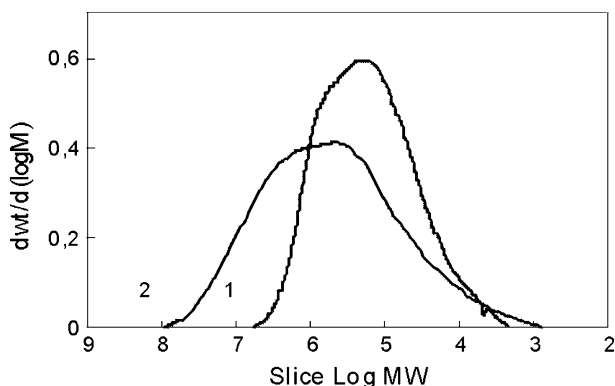


Fig. 7 Gel permeation chromatograms of ethylene/1-octene copolymers produced by $\text{VCl}_2(\text{salenCl}_2)/\text{EtAlCl}_2$ catalyst (curve 1, run 10 in Table 1) and by Sup-V/MAO catalyst (curve 2, run 29 in Table 5)

Table 5 Copolymerization results of ethylene with 1-hexene by the Sup-V

Run no.	1-Olefin (mol/l) ^a	1-Olefin (ml)	Yield (g)	Activity ^b	1-Octene content (mol%)	T_m (°C)	χ (%)
33	0.132	2.5 Hex	13.21	471.8	0.3	128.6	41.4
34	0.260	5.0 Hex	12.56	448.6	0.7	126.5	40.7
35	0.503	10.0 Hex	7.12	254.3	1.0	125.4	41.9
36	0.732	15.0 Hex	4.06	145.0	1.2	124.6	37.7
67	0.948	20.0 Hex	3.14	112.1	1.7	123.7	32.5

Copolymerization conditions: catalyst 0.028 g, activator MAO-8 mmol, Al/V = 2312, 30 min, ethylene 5 atm., temperature 30 °C, hexane 150 ml

^a 1-Octene concentration in the feed

^b Activity in g of polymer/(g cat 0.5 h)

1-octene, give the copolymer with 2.5 mol% of 1-octene units [34] whereas the copolymer produced by Sup-V/MAO at 0.579 mol/l of 1-octene contained only about 0.6 mol% of comonomer (Table 5, run 29). Both the support and the large ligand seem to create steric hindrances in the supported postmetallocene catalysts and make it hard for the bigger 1-octene molecule to reach the catalytic active site. The results shown in Table 5 show that the size of the olefin comonomer have an impact on its incorporation. The copolymer with 1.0 mol% was produced at 0.503 mol/l of 1-hexene in the polymerization feed, whereas at the similar 1-octene concentration the copolymer contained only 0.6 mol% octene units (run 35, Tables 5 and run 29, Table 4). Copolymerization experiments were conducted also for 1-decene, however, the comonomer was not incorporated into the polyethylene chain, irrespective of the 1-decene concentration content in the polymerization feed.

The results also showed that the vanadium salen-type complex after immobilization did not preferentially incorporate the 1-olefin comonomer into the polyethylene chain as compared to the titanium one (what was observed for homogeneous complexes and for supported Ziegler–Natta catalysts) [28].

Conclusion

In summary, we compared the copolymerization behaviour of vanadium and titanium complexes bearing the tetradentate Schiff base ligand. The catalytic activity in ethylene/1-octene copolymerization was strongly affected by the central metal employed ($V \gg Ti$) and a negative “comonomer effect” was observed in the process catalysed by the vanadium complex over the whole range of comonomer concentrations. In case of copolymerization with the titanium complex, additions of small amounts of the comonomer had almost no effect on the catalyst activity, while the higher 1-octene concentrations had the negative effect. Moreover, the central metal was found to be essentially decisive for comonomer incorporation and for the properties of the produced copolymers. The vanadium complex gave copolymers with clearly higher comonomer incorporation than the titanium one. The molecular weights of copolymers given by the vanadium complex were lower than those prepared by the titanium analogue and the molecular weight distributions of resultant polymers produced by $VCl_2(\text{salenCl}_2)/Et_2AlCl$ were a few times lower than available for $TiCl_2(\text{salenCl}_2)/MAO$. The M_w/M_n values for the later fell within 31–155. In addition, M_w/M_n of vanadium copolymers were almost independent on the comonomer concentration, whereas M_w/M_n of the titanium copolymers clearly increased at higher comonomer concentrations in the feed.

The vanadium complex was also found to produce more homogeneous copolymers as regards their chemical compositions, which was demonstrated with the use of the successive self-nucleation/annealing (SSA) technique to characterise the comonomer distribution in ethylene copolymers. The vanadium copolymers even with the comonomer content as high as 15 % do not undergo fractionation after applying the SSA method. This clearly indicate the presence of more types of active sites in titanium catalyst than in vanadium one.

Vanadium and titanium copolymers differ also in the microstructure of polymer chain and the dominant end groups type what in turn indicate different mechanism of copolymerization in the presence of mentioned catalytic systems.

The purpose of the work was also to compare the copolymerization behaviour of salen-type complexes and their supported counterparts. The most notable difference between the supported catalysts and their nonsupported counterparts was from the one hand their significantly higher catalytic activities and considerably higher molecular weights, and clearly inferior comonomer incorporation to the polyethylene chain on the other hand.

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