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A study of ethylene polymerization catalyzed by homogeneous and silsesquioxane supported Titanium(IV) complexes

Summary — The synthesis and characterization of titanium(IV) complexes anchored on polyhedral oligomeric silsesquioxane (POSS) and cyclohexanediol (CHD) has been investigated and compared with their unsupported analogs. These complexes were employed as catalysts for polymerization of ethylene at high temperatures in combination with organometallic aluminum compounds as co-catalysts. The influence of various reaction conditions on polymerization was discussed. The polyethylene obtained was found to be linear and displayed narrow molecular weight distribution with $\overline{M}_w$ in the range of 600—1000. The polymer was also analyzed with ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopic method which revealed a chain transfer reaction to aluminum. The unique low molecular weight PE formed in this reaction exhibits properties that have potential industrial applications in surface coating and ink formulations.

Keywords: 1,2-cyclohexanediol, cyclohexanediol-isobutyl-polyhedral oligomeric silsesquioxane, titanium(IV) complex, ethylene polymerization, organometallic aluminum compounds.

BADANIE POLIMERYZACJI ETYLENU KATALIZOWANEJ ZA POMOCĄ HOMOGENICZNYCH LUB OSADZONYCH NA NOŚNIKU SILSESKWIOKSANOWYM KATALIZATORÓW BĘDĄCYCH KOMPLEKSAMI TYTANU(IV)

Streszczenie — W ramach pracy otrzymano i scharakteryzowano kompleksy tytanu(IV) z cykloheksanodiolem (CHD) oraz cykloheksanodiolem osadzonym na nośniku, którym był poliedryczny oligomeryczny silseskwioksan (POSS). Kompleksy te zastosowano jako katalizatory do polimeryzacji etylenu w wysokich temperaturach, w połączeniu z kokatalizatorami, którymi były metaloorganiczne związki glinu. Porównano aktywność takich układów katalitycznych oraz zbadano wpływ na tę aktywność czynników, takich jak: temperatura, ciśnienie etylenu oraz rodzaj użytych rozpuszczalników. W wyniku polimeryzacji otrzymano polietylen liniowy charakteryzujący się wagowo średnim ciężarem cząsteczkowym ($\overline{M}_w$) w zakresie 600—1000. Polimer analizowano za pomocą ^{1}H NMR, ^{13}C NMR i spektroskopii FT-IR. Stwierdzono, że polietylen o tak niskich wartościach $\overline{M}_w$ wykazuje właściwości, które sprzyjają jego potencjalnym zastosowaniom, np. w produkcji różnych powłok lub tuszów.

Słowa kluczowe: 1,2-cykloheksanodiol, cykloheksanodiol-izobutyl-poliedryczny oligomeryczny silseskwioksan, kompleks tytanu(IV), polimeryzacja etylenu, metaloorganiczne związki glinu.

Olefin oligomerization/polymerization (particularly in case of ethylene) by homogeneous catalysis has been one of the most attractive subjects in the field of organometallic chemistry, catalysis and polymer chemistry because evolution of new polyolefins that have never been prepared by conventional catalysts can be highly expected by designing the new catalysts [1]. Ethylene oligomerization normally results in the formation of a range of α-olefins following a Schulz-Flory distribution. Processes based on this reaction yield olefins with an even number of carbon atoms and a more or less tunable chain length distribution. The development of efficient catalyst systems for the selective production of these olefins has been intensively studied in academia and industry since last two decades. The selective formation of light α-olefin from ethylene (for example: 1-butene, 1-hexene and 1-octene) is of particular interest because of their use in the synthesis of linear low density polyethylene. For this purpose, titanium and chromium based catalysts have attracted much attention. Homogeneous titanium catalysts play a key role in the selective dimerization of ethylene to 1-butene [2—4] whereas chromium catalysts are preferred for the formation of 1-hexene [5—10] and 1-octene [11—13].

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Industrial production of polyethylene (PE) primarily concerns conventional grades such as low density, high density and linear low density polyethylenes (PE-LD, PE-HD and PE-LLD respectively) [14, 15]. Apart from these commodity plastics, a potentially emerging segment of global polyethylene business involves the production of specialty polyethylenes, *e.g.* polyethylene wax [16, 17] and α-olefins [18, 19], which find many applications in chemical industry. As a result, catalyst systems that are more active and selective are constantly being sought to match the demands for polymer properties and minimize the production cost. PE-LD having wax-like properties is made by high pressure (free radical) polymerization or by Fischer-Tropsch route. Some by-products of PE waxes have been recently introduced. The feedstock for these materials is a mixture of PE-LD fractions and solvent, generally hexane, produced during the production of PE-HD. These waxes, however, have a wider molecular weight distribution than the PE wax synthesized directly and thus have limited end use. This means that differences among the catalysts or processes have a major impact on the use of products.

Over the last decade, polyhedral oligomeric silsesquioxane (POSS) materials have evolved as alternative supports to silica surfaces for heterogenizing homogeneous catalysts [20—23]. Commonly employed synthetic strategy for titansilsesquioxane involves direct reaction of titanocene and substituted titanocenes and alkoxides of titanium precursor compounds with silsesquioxanes. The catalytic activity of a number of Ti-POSS systems has been reported for the epoxidation of alkenes [24—26]. While the potential application of titansilsesquioxanes is yet to be fully realized they continue to attract interest due to the ease of preparation and flexibility to incorporate a large number of metal based precursors.

In a previous report half sandwich group (IV) metal chloride complexes have been anchored to cube-octameric hydroxy silsesquioxane $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ as soluble model systems for silica grafted olefin polymerization [27]. Continuing our work on novel homogeneous titanium catalysts for ethylene polymerization [28], we report herein the synthesis of titansilsesquioxane catalysts based on cyclohexanediol-isobutyl-POSS (POSS-CHD) and their evolution in catalytic ethylene polymerization in combination with organometallic aluminum compounds as co-catalysts.

EXPERIMENTAL

Materials

All manipulations were carried out under the atmosphere of nitrogen using standard Schlenk or M-Braun (Unilab) in a conventional nitrogen filled glove box technique.

Solvents were refluxed over sodium-benzophenone ketyl under the nitrogen atmosphere, distilled and kept over molecular sieves (4A).

Polymer grade ethylene (>99.95 % purity) was collected in cylinder directly from a commercial plant, the pressure of which was adjusted with a two stage regulator.

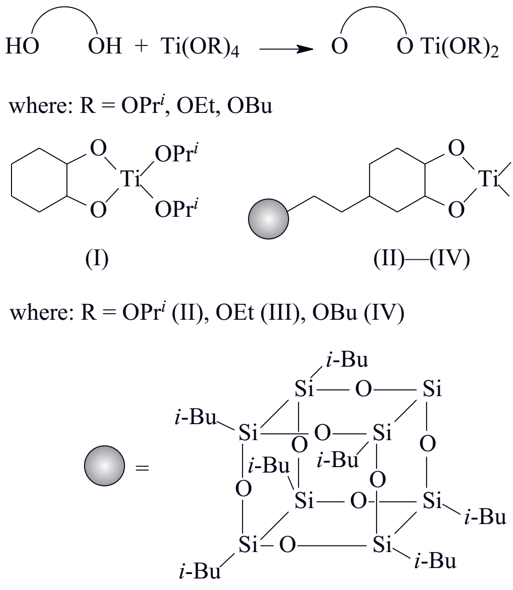
Aluminumalkyl co-catalysts, *i.e.* ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC), diethyl aluminum chloride (Et_2AlCl, DEAC), triethylaluminum (Et_3Al, TEAL) and triisobutyl aluminum [$(iso\text{-}Bu)_3Al$, TIBAL] were purchased from Ethyl Corporation while 10 % methylaluminoxane (MAO) solution in toluene was purchased from Witco GmbH. All co-catalysts were used without further purification.

Titanium tetraisopropoxide, titanium tetraethoxide, titanium tetrabutoxide, 1,2-cyclohexanediol and cyclohexanediol-isobutyl-POSS were delivered by Aldrich and were used as received.

The commercial sample of polyethylene employed in this work, MPP 635 is a micronized, high melt point, crystalline form of polyethylene which was supplied by Micro Powders, Inc. (USA). The product has melting temperature T_m = 125 °C, density at 25 °C d = 0.96 g/cm^3 and maximal particle size 31 μm. These and other grades of polyethylene waxes have been designed to increase the abrasion resistance and anti-blocking characteristics in flexographic inks as well as industrial paints and coatings.

Synthesis of catalysts

Unsupported cyclohexanediol (CHD) catalyst [formula (I) in Scheme A] was synthesized by a modified literature procedure (Scheme A) [29]. To a solution of 1.30 mmol (0.371 g) of $Ti(OPr^i)_4$ in toluene (15 cm^3) was added slowly 1.31 mmol (0.153 g) of 1,2-cyclohexanediol in toluene (15 cm^3) under the nitrogen atmosphere and



Scheme A. Unsupported and supported titanium-cyclohexane diolate catalysts heated at 100 °C for 5 h. Evaporation of solvents and volatiles yielded yellow colored complexes that were isolated by filtration, dried under vacuum and then used for ethylene polymerization. For the anchored titansilsesquioxane catalysts [formulas (II)—(IV) in Scheme A] a similar method was adopted by treating equimolar quantities of $Ti(OR)_4$ and cyclohexanediol-isobutyl-POSS (POSS-CHD).

General procedure for ethylene polymerization

Catalytic ethylene oligomerization was conducted in a 100 cm^3 stainless steel stirred autoclave (Model 4593 Parr, USA) connected to a process controller (model 4871) and operated through a microprocessor controller (PC/PLC) using a customized Honeywell specview32 software. Prior to polymerization, the reactor was baked to 150 °C under nitrogen pressure (~0.98 MPa) for 2 h and cooled down to the ambient temperature. In a typical experiment catalyst (I) (2 mg, $7.14 \cdot 10^{-6}$ mol) dissolved in toluene (20 cm^3) and EASC (0.88 g, $3.53 \cdot 10^{-3}$ mol) in toluene (20 cm^3) were carefully charged into the reactor under a nitrogen blanket. The Al/Ti molar ratio was kept at 500. The reactor was gradually heated to 100 °C and then pressurized with ethylene to 2.068 MPa, continued for 1 h, cooled, the excess ethylene was degassed and the slurry slowly poured into acidic methanol (5 vol. %) to precipitate the polymer. The white polyethylene powder was filtered, washed several times with methanol followed by acetone and finally dried under reduced pressure at 60 °C for 1 h.

Analytical techniques

Microanalysis was carried out on a Perkin Elmer model 2400 instrument. Titanium contents of catalysts were determined gravimetrically as TiO_2.

FT-IR spectra of the catalysts were recorded in KBr on a Nicolet 6700 FT-IR spectrometer. The FT-IR spectra of polymers were recorded by pressing the polyethylene powder into 0.5 mm thick pellets and scanning in the region between 400 and 4000 cm^{-1} with 0.5 cm^{-1} resolution for 16 scans.

^1H NMR spectra of catalysts were recorded on a Brüker 500 MHz instrument using C_6D_6 as solvent. The ^{13}C NMR and ^1H NMR spectra of polymer samples were recorded on an Ultrashield Brüker 400 MHz spectrometer at 110 °C. The solutions were made up in *o*-dichlorobenzene-d_4. For the ^{13}C NMR spectra the chemical shifts were referenced internally to the major backbone methylene carbon resonance which was taken to be 30.00 ppm. For the ^1H NMR spectra the chemical shifts were referenced to residual H solvent shifts at 7.249.

Molecular weights of polymer were determined by size exclusion chromatography. The high temperature gel permeation chromatography (GPC) analysis of the polymers was carried out with Polymer Lab's PL-GPC 220 chromatograph. A set of three PL Gel Mixed B columns was used. 1,2,4-Trichlorobenzene was used as the mobile phase at 145 °C. 0.0125 % of Irganox was added to the mobile phase before filtration. A sample preparation unit, PL-SP260, was used to dissolve and filter the samples at 145 °C. 0.2 % solutions were injected using an auto sampler to record the chromatogram. Viscotek's Trisec conventional software was used to analyze the chromatograms, which were matched with polystyrene calibration curve. The following MHK constants were used to construct a universal calibration curve:

— for polystyrene, $K = 1.2105\ e^{-4}$ and $a = 707$;
— for PE, $K = 4.055\ e^{-4}$ and $a = 725$.

Differential scanning calorimetry (DSC) was performed under continuous nitrogen purge on a Mettler-Toledo DSC 822 instrument from 30 to 200 °C at the scan rate of 10 deg/min. Indium was used to perform calibration of the equipment.

XRD measurements were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni filled CuKα radiation (λ = 1.5406 Å, generator voltage = 45 kV, current = 40 μA) in the reflection mode, as detected by a scintillation counter. Samples were pressed films approximately 400 μm thick and they were scanned into 2θ ranges from 15 to 45° at the rate of 1°/min. Measurements were recorded at steps of 0.02°.

Scanning electron micrographs (SEM) of powdered polymer samples were taken on Jeol JFC 1100 instrument ion sputter water. They were observed in a Jeol 5600 CV scanning electron microscope in the Hv mode at the operating voltage of 20 kV.

RESULTS AND DISCUSSION

Characterization of catalysts

The synthesis of soluble complexes Ti(IV) could be realized by the stoichiometric reaction between $Ti(OPr^i)_4$ and CHD or POSS-CHD ligand. Catalysts (I)—(IV) were stable at the room temperature under inert atmosphere and were yellow colored complexes. The titanium complexes described by the empirical formula $Ti(CHD)(OPr^i)_2$ or $Ti(POSS\text{-}CHD)(OR)_2$ are generally soluble in aromatic and chlorinated aromatic solvents but only sparingly in aliphatic hydrocarbons.

The results of elemental and ^1H NMR analysis of prepared catalysts are given in Table 1.

The ^1H NMR spectra are generally simple and were primarily used as a diagnostic tool to ascertain the purity of complexes. In the ^1H NMR of catalyst (I), the multiplets peak occurs at 1.13—1.15 ppm for **C**H_3 protons of isopropyl group, another multiplet peak occurs at 1.49—1.53 ppm for **C**H_2 protons of the cyclohexyl, a single peak occurs at 2.31 ppm for **CH** protons of cyclohexyl and multiplet peak at 3.97—3.99 ppm for C**H** protons of isopropyl group. In the ^1H NMR a signal at 3.69 ppm in

Table 1. Characteristics of synthesized catalysts

Catalyst	Formula of catalyst	Yield of synthesis, %	Results of elemental analysis		Results of ^{1}H NMR analysis
			calculated	found	
(I)	$C_{12}H_{24}O_4Ti$	79	C 51.44 % H 8.63 % Ti 17.08 %	C 52.16 % H 9.02 % Ti 16.94 %	($CDCl_3$): 1.13—1.15 (12H, CH-**Me**$_2$), 1.43—1.53 (8H, C**H**$_2$ of cyclohexyl), 2.31 (2H, C**H** of cyclohexyl), 3.97—3.99 (2H, C**H**-Me$_2$)
(II)	$C_{42}H_{90}O_{16}Si_8Ti$	45	C 44.95 % H 8.07 %	C 45.29 % H 8.25 %	(C_6D_6, 25 °C): 1.07—1.11 (42H, **Me**$_2$ of *i*-Bu and 12H, O-CH-**Me**$_2$), 0.82—0.87 (16H, Si-C**H**$_2$, 2H, Si-CH$_2$-C**H**$_2$ bridge and 6H, -C**H**$_2$ of cyclohexyl), 2.08—2.12 (7H, C**H** of *i*-Bu and 3H, -C**H** of cyclohexyl group), 4.17 (2H, O-C**H**-Me$_2$)
(III)	$C_{40}H_{86}O_{16}Si_8Ti$	44	C 43.85 % H 7.91 %	C 43.33 % H 7.69 %	(C_6D_6, 25 °C): 1.05—1.10 (42H, **Me**$_2$ of *i*-Bu and 6H, O-CH$_2$-**Me**), 0.84—0.88 (16H, Si-C**H**$_2$, 2H Si-CH$_2$-C**H**$_2$ bridge and 6H, -C**H**$_2$ of cyclohexyl), 2.07—2.10 (7H, -C**H** of *i*-Bu and 3H, -C**H** of cyclohexyl), 3.59—3.61 (4H, O-C**H**$_2$-Me)
(IV)	$C_{44}H_{94}O_{16}Si_8Ti$	46	C 45.88 % H 8.23 %	C 44.65 % H 7.95 %	(C_6D_6, 25 °C): 1.08—1.14 (42H, **Me**$_2$ of *i*-Bu and 6H, CH$_2$-**Me**$_2$), 0.79—0.85 (16H, Si-C**H**$_2$, 2H, Si-CH$_2$-C**H**$_2$ bridge, 8H, (C**H**$_2$)$_2$-Me of butyl and 6H, -C**H**$_2$ of cyclohexyl), 2.08—2.11 (7H, CH$_2$-C**H** and 3H, -C**H** of cyclohexyl group), 3.60—3.63 (4H, O-C**H**$_2$)

ligand was assigned to the -O**H** protons. The absence of -O**H** protons at 3.69 ppm in the catalyst (I) indicates complete deprotonation of the diol and attachment to the titanium alkoxide.

Catalysts (I)—(IV) were also characterized by FT-IR, thermogravimetric analysis and mass spectrometry. In the FT-IR spectrum of catalyst (I) a broad peak observed in 3000—3500 cm^{-1} indicates the deprotonation of the diolate ligands.

In the mass spectrum of catalyst (I) molecular ion peak M$^+$ of the parent complex appeared at 281 (calculated 280) which corresponds to the Ti-(CHD)(OPr^i)$_2$ species. However, the parent ion of the cyclohexane diolate ligand was not detected in the mass spectrum but the molecular ion peak at 166 (calculated 166) was observed for (M-diolate)$^+$ species.

The thermal degradation profile of catalyst (I) shows a peak at 309 °C corresponding to the loss of diolate — 37.48 % (calculated 40.71 %). With increasing temperature a peak at 404 °C is assigned to the loss of isopropyl groups — 30.48 % (calculated 30.71 %) and with further increase of the temperature another peak at 499 °C shows a complete degradation to TiO_2 (observed 28.83 %, calculated 28.57 %) for this catalyst.

Catalytic ethylene polymerization

The newly prepared complexes were examined for ethylene polymerization. The characteristics of products of ethylene polymerization ($\overline{M}_w$ — weight-average molecular weight, Đ — dispersity, T_m — melting temperature) obtained using the Ti(IV) catalysts (I)—(IV) is compiled in Table 2. Ethylene polymerization was investigated under different reaction conditions such as temperature, pressure, solvent and co-catalysts. Initial examination of catalysts indicates that unsupported catalyst (I) showed higher activity than POSS supported catalysts (II)—(IV). On the other hand comparison with the benchmark metallocene (Cp_2TiCl_2) showed it to be inactive under similar reaction condition. The activity was predominantly dependent on the nature of the co-catalyst as shown in Table 3. It is clear that EASC was found to promote ethylene polymerization. Other chlorinated alkylaluminum compound such as DEAC was also active but catalyst productivity was lower. In the case of the conventional co-catalyst for polyolefin production such as TEAL and methylaluminoxane (MAO), only the latter showed moderate activity with the isolated PE being largely coarse and inhomogeneous. While the remarkable activity with EASC needs further investigation it is reasonable to assume that the Lewis acidity of halogenated alkylaluminum plays a significant role in polymerization compared to TEAL and MAO.

Table 2. Comparison of the results of ethylene polymerization at 100 °C using various Ti-diolate-EASC catalyst systems (ethylene pressure 2.068 MPa, reaction time 1 h, molar ratio Al/Ti = 500)

Catalyst	Productivity kg PE/g Ti	$\overline{M}_w$	Đ	T_m, °C	Crystallinity, %	
					XRD	DSC
(I)	23.1	639	1.4	121	74.9	75.7
(II)	11.7	829	1.6	125	75.4	76.1
(III)	9.2	723	1.5	123	73.7	74.1
(IV)	7.2	941	1.5	122	74.2	73.8
Cp_2TiCl_2	5.9	20 800	5.0	132	73.0	75.1

Detailed studies on the effect of temperature and pressure were then carried out with catalyst (I) in the presence of EASC as co-catalyst. From the results presented in Figure 1 it is evident that increase in the reaction temperature from ambient to 100 °C has an apparent effect on the catalyst activity. Further increase in the reaction temperature (120 °C), however, showed marginal reduction in

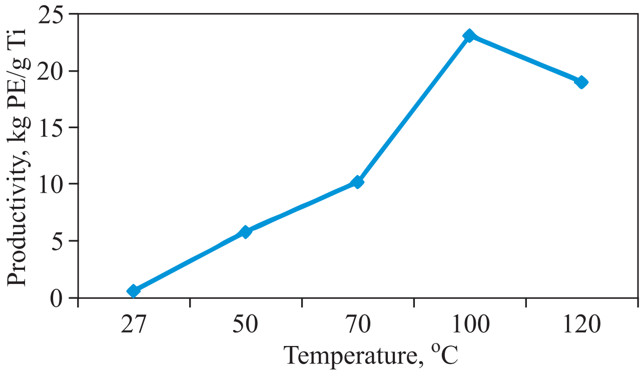


Fig. 1. Influence of temperature on productivity of ethylene polymerization

productivity. The slight decrease in activity at high temperatures could be due to the deactivation of the active species. The effect of ethylene pressure on polymerization is compiled in Table 4. Applying higher ethylene pressure led to higher productivity.

Table 3. Effect of co-catalyst on ethylene polymerization at 100 °C (ethylene pressure 2.068 MPa, reaction time 1 h, molar ratio Al/Ti = 500)

Co-catalyst	Productivity, kg PE/g Ti	
	catalyst (I)	catalyst (II)
EASC	23.1	11.7
DEAC	7.8	2.4
MAO	0.4	0.6
TEAL	0.3	0.4
TIBAO	—	—

Table 4. Influence of pressure on ethylene polymerization at 100 °C (reaction time 1 h, mole ratio Al/Ti = 500)

Pressure, MPa	Productivity, kg PE/g Ti	
	catalyst (I)	catalyst (II)
2.758	30.4	16.6
2.068	23.1	11.7
1.379	15.0	3.9
0.689	4.0	0.5

Table 5. Influence of solvent on ethylene polymerization (ethylene pressure 2.068 MPa, reaction time 1 h, molar ratio Al/Ti = 500)

Solvent	Productivity, kg PE/g Ti	
	catalyst (I)	catalyst (II)
Toluene	23.1	11.7
Chlorobenzene	32.3	18.3
Cyclohexane	0.4	—
n-Hexane	0.3	0.6

A brief examination of how different solvents affect the polymerization was performed. The results collected in Table 5 indicate that chlorinated aromatic solvent such as chlorobenzene showed an increase of about 40 % in productivity for catalyst (I) and 56 % for catalyst (II) compared to toluene. A plausible explanation stems from the fact that the putative cationic catalytic species may compete for co-ordination by the monomer as well as by toluene to form the η^6 complex with the metal center [30]. Such competitive binding by monomer may not exist with electron-deficient chlorobenzene, thus allowing for a more productive polymerization reaction in the medium. The increased activity in chlorobenzene could also be attributed to the high dielectric constant of the medium. Other hydrocarbon solvents such as cyclohexane and *n*-hexane showed poor activity under these reaction conditions.

A noteworthy feature of the PE obtained with Ti-CHD and Ti-POSS-CHD catalysts was the invariably low molecular weight of the polymers as revealed by GPC analysis. In all cases, the PEs displayed narrow molecular weight distributions (Đ = 1.4—1.6). However, monosubstituted tetra-aryloxides of Ti such as $Ti(OR)_4$ essentially lead to low molecular weight linear α-olefins in the $C_4—C_{20}$ carbon range which is in sharp contrast to the exclusive formation of solid PE with sterically bulky bidentate $Ti(O^\wedge O)_2$ type complexes used in this study [31]. This can be qualitatively interpreted as chain propagation and termination rates are similar ($r_p \approx r_t$) in the case of the $Ti(OR)_4$-EASC catalyst system which resulted in oligomer formation, whereas with the Ti-CHD-EASC system, $r_p > r_t$, gave PE under identical conditions.

The properties of PEs were characterized by GPC and were reported in Table 2. GPC clearly indicates low molecular weights of the materials, *i.e.* $\overline{M}_w = 639—1036$. In no case was high molecular weight polyethylene ($\overline{M}_w \geq 10^5$) obtained though these catalysts resemble typical Ziegler systems. The DSC reveals lower T_m values than those observed for conventional PE-HD or PE-LD. PEs obtained using catalyst (I)—(IV) showed a higher crystallinity (70—76 %) as computed from specific heat of fusion determined by DSC (Figure 2). For comparison of polymer properties obtained in this work, a commercial sample of micronized PE wax powder (MPP-635) was included [32]. The crystalline nature was also supported by intense reflections for the orthorhombic phase at 2θ = 21.7° and 24.0° respectively in the XRD (Figure 3). $T_m = 121—125$ °C are lower compared to commercial PE-HD (T_m = 128—135 °C). The isolated PEs after polymerization have the form of fine particles and uniform morphology as seen by scanning electron micrograph (SEM). A typical SEM is reproduced in Figure 4.

^1H NMR, ^{13}C NMR and FT-IR spectroscopic methods were used to analyze the microstructure of polyethylene. In the ^1H NMR spectra of PE, presented in Figure 5, a strong signal at 1.33 ppm and a signal of lower intensity at 0.90 ppm were observed, which are ascribed to the

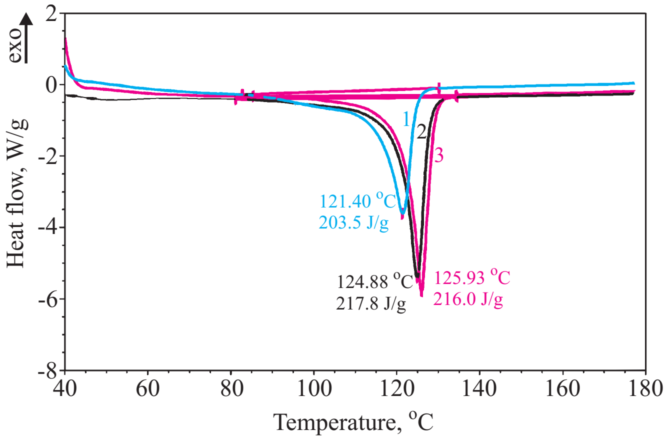
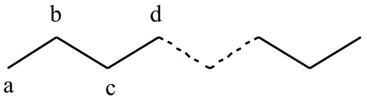


Fig. 2. DSC curves of PEs synthesized using catalyst (I) (1), catalyst (II) (2), and commercial sample of MPP-635 (3)



(V)

main chain methylene protons $(\text{-C}\mathbf{H}_2\text{-})_n$ and to the methyl end group protons $(\text{-C}\mathbf{H}_3)$, respectively. However, the intensity of the methyl resonance was significantly lower with respect to that of the main chain methylene protons [33, 34]. The ^{13}C NMR spectra presented in Figure 6 showed a strong signal at 30.0 ppm (d) for the main chain methylene carbons $(\text{-}\mathbf{C}\text{H}_2\text{-}\mathbf{C}\text{H}_2)_n$ of PE and lower intensity signals at 14.10 ppm (a) for $\mathbf{C}\text{H}_3$, 22.85 ppm (b) for α-$\mathbf{C}\text{H}_2$ and 32.18 ppm (c) for β-$\mathbf{C}\text{H}_2$ which are ascribed to the chain ends [formula (V)] [35, 36]. The absence of signals ascribed to olefinic protons and carbons indicates that obtained PE is highly linear in nature.

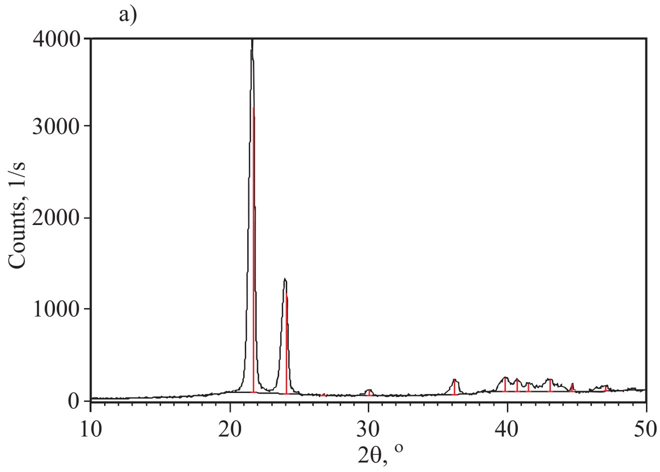


Fig. 3. XRD spectrum of PEs obtained using catalyst (I) (a) and catalyst (II) (b)

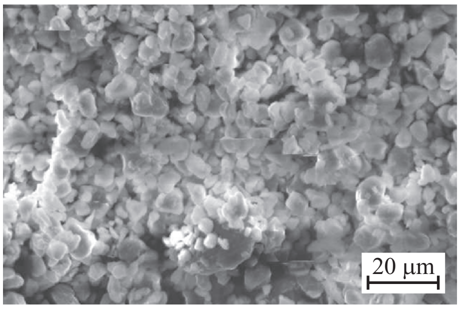


Fig. 4. SEM image of PE obtained using catalyst (I)

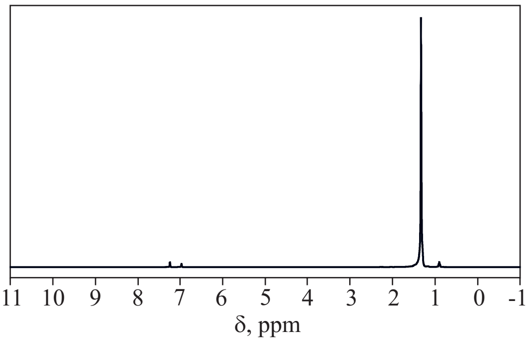


Fig. 5. ^{1}H NMR spectrum of PE synthesized using catalyst (I)

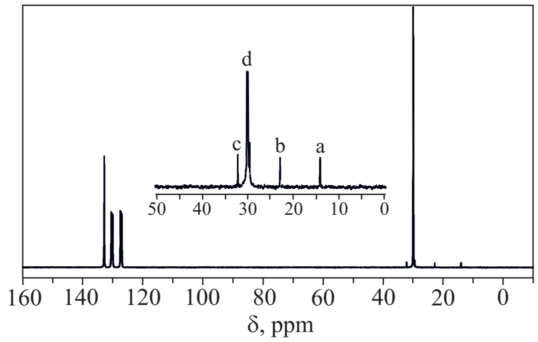


Fig. 6. ^{13}C NMR spectrum of PE synthesized using catalyst (I)

As a benchmark for comparison the ^{1}H NMR and ^{13}C NMR spectra of commercial sample MPP-635 were studied and were shown in Figure 7. Both ^{1}H NMR and ^{13}C NMR spectra of MPP-635 were similar to the spectra of PE obtained with catalyst (I).

In the FT-IR spectrum of polymer the peaks at 2919, 2849 and 1469 cm^{-1} were assigned to the C-H and C-C absorption. The peak at 722 cm^{-1} is ascribed to the long

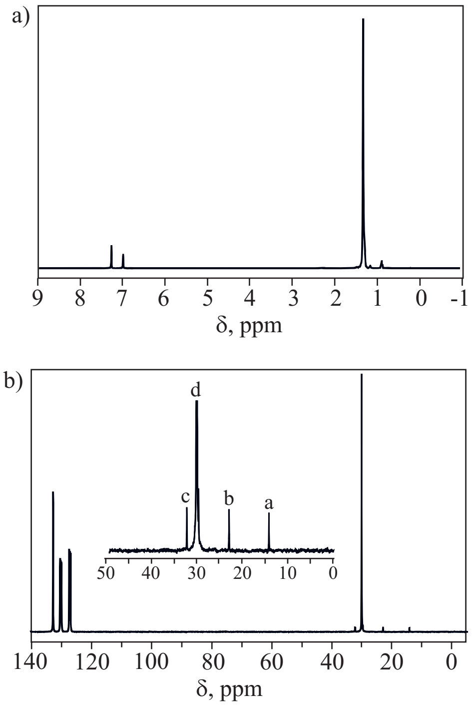


Fig. 7. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of commercial sample of MPP-635

chain alkane, which arises from the rocking of methylene group perpendicular to the chain direction. The presence of this band arises from crystalline region and provides evidence for linearity of the polymer [37].

The NMR and FT-IR results exhibited no features corresponding to branching or C=C linkages that arise from transfer or termination reactions. The linear and saturated molecular structure of the polyethylene indicates that chain walking that is closely linked to β-H elimination or β-H transfer is disfavored. ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopic data suggest that chain transfer to aluminum of EASC was predominant in catalytic reaction leading to low molecular weight polymer [38, 39].

The low molecular weight and narrow dispersity of PE obtained with these catalyst systems are likely to find applications as dispersing agents in coatings and ink formulations. Detailed kinetic studies of this reaction are underway.

Reaction mechanism

Reaction of Ti(OR)$_4$ with alkylaluminum halides has been reported to yield active intermediates responsible for the polymerization of ethylene to low molecular weight products [40].

Since $Et_3Al_2Cl_3$ (EASC) can dissociate as Et_2AlCl (DEAC) and $EtAlCl_2$ in solution, it is reasonable to expect the formation of two types of catalytic species on interaction with Ti-CHD or Ti-POSS-CHD catalyst. The reduction of Ti(IV) in the presence of EASC will generate catalytically active components. The active catalysts in polymerization need to retain monomeric four or five coordinate geometry to allow for olefin insertion and subsequent propagation [41]. In the Ti-CHD or Ti-POSS-CHD catalytic system higher temperature tends to favor formation of active intermediates responsible for ethylene polymerization.

Though the structure of active intermediate is yet unknown the mechanism leading to polyethylene is consistent with those reported previously for solution phase olefin polymerization using titanium alkoxides and aluminum alkyls [42, 43]. Efforts are underway to investigate the detailed kinetics of this reaction and catalyst activity.

CONCLUSIONS

The complexes of Ti(IV) with diolate ligand act as efficient catalysts in the presence of ethylaluminum sesquichloride as a co-catalyst for the synthesis of specialty low molecular weight polyethylene with high productivity. The physical properties exhibited by these PEs such as low molecular weight, high crystallinity and narrow dispersity suggest single-site catalytic behavior of these Ti(IV) precursors. The close resemblance of polymer properties to commercially important synthetic waxes holds promise for developing alternative cheaper catalysts for this process.

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