



# Effect of $\text{AlR}_3$ (R = Me, Et, *i*Bu) addition on the composition and microstructure of ethylene/1-olefin copolymers made with post-metallocene complexes of group 4 elements

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Received: 29 May 2018 / Revised: 17 July 2018 / Accepted: 30 July 2018 / Published online: 7 September 2018  
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## Abstract

The effect of trialkylaluminum compound ( $\text{AlR}_3$ , where R = Me, Et, *i*Bu) addition on the performance of the  $[\text{LigZrCl}]_2$  ( $\mu\text{-O}$ )/ $\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  and  $\text{LigTiCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  (Lig =  $\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{-}2\text{-O-}3,5\text{-}i\text{Bu}_2\text{-C}_6\text{H}_2)_2$ ) catalysts in ethylene/1-olefin copolymerization was investigated. The presence of  $\text{AlMe}_3$  in the feed during the copolymerization process catalyzed by the diamine-bis(phenolate) zirconium catalyst greatly increases the amount of incorporated comonomer and leads to microstructural changes, e.g., the formation of blocky and alternating sequences of 1-olefin units. Moreover, the use of  $\text{AlMe}_3$  limits the reaction yield and decreases the molecular weight of the produced copolymers. The catalytic properties of the diamine-bis(phenolate) titanium catalyst were much less affected by trimethylaluminum; its use slightly decreased the catalyst activity and copolymer molecular weight. A lower molecular weight was also detected for the copolymers produced by catalysts in the presence of both  $\text{AlEt}_3$  and  $\text{Al}i\text{Bu}_3$ , whereas they did not cause any important changes in the catalytic activity, overall composition or microstructure of the produced copolymers. Copolymerization tests with other catalytic systems,  $(\text{Lig}^{\text{FI}})_2\text{ZrCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  ( $\text{Lig}^{\text{FI}} = (\text{C}_6\text{H}_5)_2\text{N} = \text{CH}(2\text{-O-}3,5\text{-}i\text{Bu}_2\text{-C}_6\text{H}_2)$ ) and  $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MMAO}$ , in the presence of  $\text{AlMe}_3$ , were also carried out for the purpose of comparison.

## Introduction

The synthesis of ethylene/1-olefin copolymers with the desired microstructures and properties by controlling the comonomer incorporation and distribution along the polymer chains is an important area of current research. The common approach in pursuing this goal is to design suitable catalysts, primarily by modifying the ancillary ligands of transition metal complexes [1–4]. One of the most important achievements in recent years in this field has been the development of transition metal complexes

for living alkene copolymerization. They make it possible to obtain olefin copolymers with microstructures that were unattainable for a long time, such as well-defined poly-olefin-based diblock and multiblock copolymers [5, 6]. The chain shuttling copolymerization permits researchers to obtain a new class of multiblock copolymers with sequential crystallizable and non-crystallizable statistical copolymer segments through the sequential growth of the polymer chains on two different catalysts, with the use of a chain shuttling agent, typically alkylaluminum or alkyl-zinc [7, 8]. The same organometallic compounds are used as chain transfer agents (CTA) in the coordinative chain transfer copolymerization (CCTcoP) involving the use of only one catalyst [7, 8]. Such a method can increase the catalyst efficiency and allow for better control of the molecular weight and composition of statistical copolymers [9]. The CCTcoP of ethylene with 1-alkenes has not been explored much to date [7, 10–12]. The ethylene/1-hexene copolymerization with the pyridyl-amide hafnium catalyst and  $\text{AlOct}_3$  as CTA [13] and living copolymerization of ethene with 1-hexene and 1-octene catalyzed by the monocyclopentadienyl amidinate hafnium catalyst in

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1038/s41428-018-0117-8>) contains supplementary material, which is available to authorized users.

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combination with  $\text{ZnEt}_2$  have been reported [10]. The comonomer incorporation was found to change only slightly with the increasing amount of CTA, and the comonomer was almost exclusively incorporated as isolated units [10]. Conversely, the chain transfer increased the quantity of 1-hexene in poly(styrene-co-hexene) copolymers that were obtained with  $\text{Cp}^*\text{La}(\text{BH}_4)_2(\text{THF})_2/\text{n-BuEtMg}$  [9] and the quantity of norbornene in ethylene/norbornene copolymers produced by the metallocene catalysts in combination with  $\text{AlR}_3$  or  $\text{ZnR}_2$  [14]. On the other hand, for most catalytic systems, the growing macromolecules are transferred non-reversibly from the active site to the organoaluminum compound. Just like the reversible chain transfer, this reaction leads to lower (co) polymer molecular weights [15, 16]. If the catalyst predominantly undergoes the chain transfer to aluminum, Al-terminated polyethylenes are formed, which can be useful precursors for end-functionalized PEs [17, 18].

Consequently, we were interested in investigating whether and how the ethylene/1-olefin copolymerization, catalyzed by the post-metallocene catalytic systems, can be influenced by the addition of  $\text{AlR}_3$  to the polymerization feed. We selected catalysts that were based on zirconium and titanium complexes bearing the diamine-bis(phenolate) ligand (Fig. 1). The zirconium complex  $[\text{LigZrCl}_2]_2(\mu\text{-O})$  in combination with  $\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  was previously found to be highly active in ethylene/1-octene copolymerization and to possess a high ability to incorporate the comonomer [19]. Good incorporation ability was exhibited by a similar titanium complex,  $\text{LigTiCl}_2$ , as well [19]. To verify whether their catalytic behavior could be modified by the alkylaluminum compound, in the present work, we studied the effect of different trialkylaluminum compounds ( $\text{R} = \text{Me}, \text{Et}, i\text{Bu}$ ) addition on the catalyst activity and on copolymer properties and microstructure. For purposes of comparison, analogous studies were performed in the presence of  $(\text{Lig}^{\text{FI}})_2\text{ZrCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ , where  $\text{Lig}^{\text{FI}}$  = phenoxy-imine ligand, and the metallocene catalyst  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  (Fig. 1).

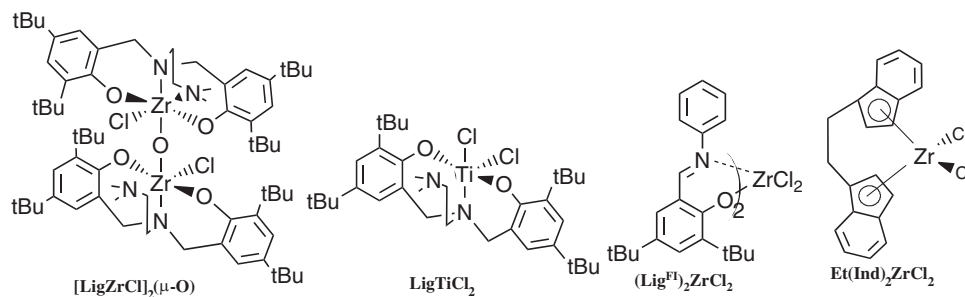
## Experimental procedure

### Materials and methods

1-Octene (99.0%+) and 1-hexene (97.0%) from Acros Organics and benzene- $d_6$  (99.6 atom% D) from Aldrich were dried under argon over A4 molecular sieves. Toluene (ACS grade, Chempur) and hexane (Stanlab) were refluxed in a nitrogen atmosphere over sodium and sodium/benzophenone, respectively. Ethylene (3.0 grade, Linde Gas) was passed through a column with sodium metal deposited on  $\text{Al}_2\text{O}_3$ . Argon (5.0 grade, Linde Gas),  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  (Aldrich), MMAO (7 wt % in toluene, Aldrich),  $\text{Al}i\text{Bu}_3$  (1 M in toluene, Aldrich),  $\text{AlMe}_3$  (2 M in toluene, Witco),  $\text{AlEt}_3$  (1.9 M in toluene, Aldrich),  $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  (97%, abcr GmbH & Co. KG), 1,2-dichlorobenzene- $d_4$  (98.0 atom% D, Aldrich), and 1,2,4-trichlorobenzene (TCB) (99.0%, Acros Organics) were used as received.

The molecular weights of the (co)polymers were determined by gel permeation chromatography (GPC) with an Alliance 135 GPCV 2000 device equipped with HT3 and HT6E columns. Measurements were conducted using 1,2,4-trichlorobenzene as a solvent, with flow rate of 1.0 mL/min, at 135 °C. The calibration curve was obtained with narrow molecular weight polystyrene standards with a range of  $1.0 \times 10^3$  to  $3.7 \times 10^6$  g/mol. DSC analyses were performed using a 2010 DSC calorimeter from TA Instruments. Thermograms were recorded at a heating rate of 10 °C/min for samples that were melted and crystallized to erase any thermal history.  $^{13}\text{C}$  NMR experiments were carried out on a 400 MHz Ultrashield Bruker spectrometer. Copolymers were dissolved in 1,2-dichlorobenzene- $d_4$ /TCB at 120 °C. The peak with the highest intensity was referenced to 30.00 ppm, and only in the case of copolymer 5, with the highest 1-octene content, was a peak for 14.05 ppm derived from methyl carbon in the side chain used as an internal standard. The comonomer content was calculated from the  $^{13}\text{C}$  NMR spectra as the ratio of the intensity of the branched carbon(s) signal ( $2 \cdot \Sigma I_{\text{CH}}$ ) to the intensities of the backbone carbon signals.  $^1\text{H}$  NMR

**Fig. 1** Structures of the early transition metal complexes used in this work



spectra of complexes were obtained at room temperature in benzene-d<sub>6</sub> and referenced to internal solvent resonance.

## Synthesis of complexes

Diamine-bis(phenolate) complexes of M(IV) (Zr, Ti), [LigZrCl]<sub>2</sub>(μ-O) and LigTiCl<sub>2</sub>, were prepared in accordance with procedure described in [20, 21]. [LigZrCl]<sub>2</sub>(μ-O), <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.51 (d, 4 H, Ar-H), 7.06 (d, 4 H, Ar-H), 5.27 (d, 4 H, NCH<sub>2</sub>Ar), 3.23 (d, 4 H, NCH<sub>2</sub>Ar), 2.21 (m, 4 H, CH<sub>2</sub>), 1.84 (s, 12 H, N(CH<sub>3</sub>)<sub>2</sub>), 1.50 (m, 4 H, CH<sub>2</sub>), 1.44 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.42 (s, 36 H, C(CH<sub>3</sub>)<sub>3</sub>). LigTiCl<sub>2</sub>, <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.60 (d, 2 H, *J* = 2.3 Hz), 6.96 (d, 2 H, *J* = 2.3 Hz), 4.35 (d, 2 H, *J* = 13.8 Hz, NCH<sub>2</sub>Ar), 2.78 (d, 2 H, *J* = 14.4 Hz, NCH<sub>2</sub>Ar), 2.11 (m, 2 H, CH<sub>2</sub>), 1.90 (s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>), 1.80 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.61 (m, 2 H, CH<sub>2</sub>), 1.39 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>).

## General procedure for ethylene homo- and copolymerization

Ethylene/1-octene copolymerizations were carried out in a 500 mL Büchi glass autoclave equipped with a magnetic stirrer and heating/cooling mantle. Hexane (100 mL) and comonomer (5 mL) were sequentially added to the autoclave and then saturated with ethylene at a pressure of 5 bar, at the required temperature. After the autoclave was degassed, Al*i*Bu<sub>3</sub>, complex solution, Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> solution (both in toluene) and AlR<sub>3</sub> (R = Me, Et, *i*Bu) were introduced (the total volume of liquids in the reactor was equal to 120 mL). It was immediately pressurized to 5 bar. The monomer pressure and temperature were kept constant throughout the run. After 30 min, the reaction was quenched by adding 200 mL of a dilute solution of hydrochloric acid in methanol. The polymeric product was filtered off, washed with methanol and dried in air and then in a vacuum oven at 45 °C. Ethylene homopolymerization was carried out as described for copolymerization, except the higher 1-olefin was not inserted into the reactor.

## Thermal fractionation

The thermal fractionation of copolymers was performed according to the self-nucleating annealing (SSA) procedure [22] using DSC calorimeter from TA Instruments. Initially, to erase a thermal history, a sample was heated from 0 °C to 170 °C, held at this temperature for 20 min and then cooled down to 0 °C. Next, the sample was heated at a rate of 5 °C/min up to the first selected temperature *T*<sub>s</sub>, 140 °C, and kept for 20 min at this temperature before cooling to 0 °C at the same rate of 5 °C/min. This procedure was then repeated with lower *T*<sub>s</sub>

temperatures. The chosen *T*<sub>s</sub> range was from 140 to 68 °C; only for copolymer 7; this range was wider, from 140 to 29 °C. The intervals between consecutive *T*<sub>s</sub> were equal to 3 °C.

## Results and discussion

### Effect of AlR<sub>3</sub> on catalytic properties of [LigZrCl]<sub>2</sub>(μ-O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>

The results of ethylene/1-olefin polymerizations catalyzed by [LigZrCl]<sub>2</sub>(μ-O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, which were conducted in the presence of different alkylaluminum compounds and, for comparison, without such compounds, are presented in Table 1. The copolymerization reactions were performed under identical conditions, i.e., at 60 °C, under 5 bars of ethylene, for 30 min. In each case, 5 mL of 1-octene or 1-hexene (0.27 and 0.33 mol/L, respectively) were used as a comonomer. However, initially, ethylene was subjected to homopolymerization, and the polymer with a yield equal to 2.150 g and *T*<sub>m</sub> = 128.2 was obtained (run 1). The use of 1-octene in the polymerization feed (run 2), as expected [19], resulted in a better catalytic activity due to the positive comonomer effect. The formed copolymer was characterized by a high comonomer incorporation level (10.0 mol%). When AlMe<sub>3</sub> was added at the

**Table 1** Results of ethylene homopolymerization and ethylene/1-olefin copolymerization with [LigZrCl]<sub>2</sub>(μ-O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>

Run	1-olefin	AlR <sub>3</sub> : Zr [mol/ mol]	Yield [g]	Activity [kg/ (mol <sub>Zr</sub> ·h)]	M <sub>w</sub> [g/ mol]	Đ	[O] (or [H]) [mol %]
1	—	—	2.150	86.0	nd	nd	—
2	1-octene	—	10.530	421.2	64,800	3.0	10.0
3	1-octene	100:1	0.707	28.3	15,800	5.5	39.5
4 <sup>a</sup>	1-octene	100:1	9.712	388.5	4900	3.8	8.1
5	1-octene	150:1	1.117	44.7	11,100	6.8	64.6
6	1-octene	25:1	2.499	100.0	nd	nd	18.3
7 <sup>b</sup>	1-octene	100:1	8.762	350.5	10,000	7.6	10.6
8	1-hexene	—	17.314	692.6	50,300	5.8	7.9
9	1-hexene	100:1	1.386	55.4	5360	4.0	30.5
10 <sup>a</sup>	1-hexene	100:1	12.490	499.6	nd	nd	10.0
10A <sup>b</sup>	1-hexene	100:1	17.457	698.3	nd	nd	7.4

Copolymerization conditions: 0.050 mmol of Zr, 0.075 mmol of Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, 0.75 mmol of Al*i*Bu<sub>3</sub>, 60 °C, 30 min, 5 bar of ethylene, 5 mL of 1-olefin, AlR<sub>3</sub> = AlMe<sub>3</sub>

nd not determined

<sup>a</sup>AlR<sub>3</sub> = AlEt<sub>3</sub>

<sup>b</sup>AlR<sub>3</sub> = Al*i*Bu<sub>3</sub>

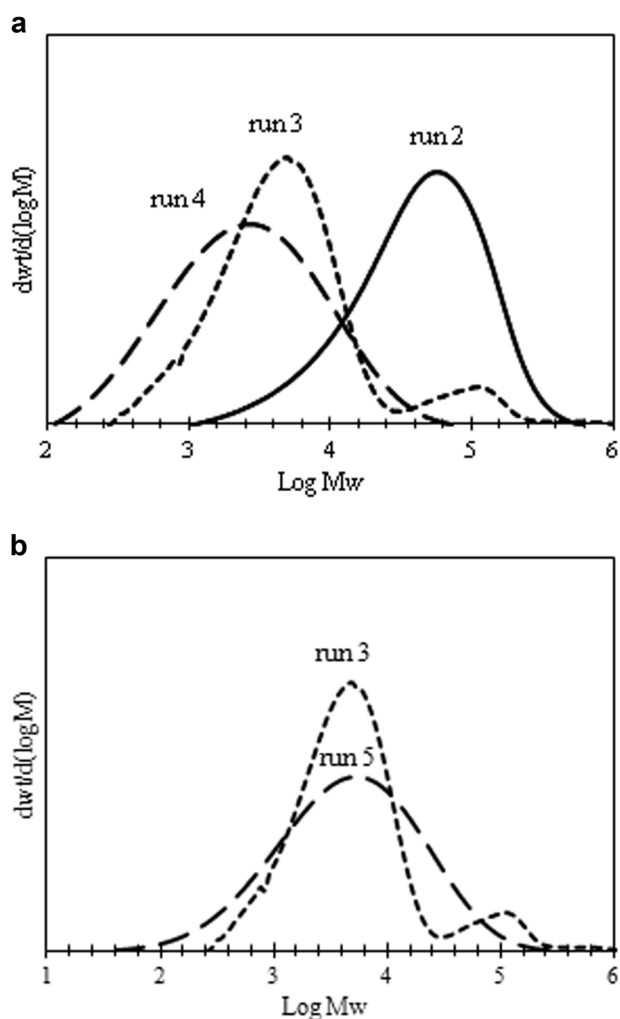
100:1 molar ratio (run 3), under the same copolymerization conditions as run 2, the catalyst activity significantly decreased, and the comonomer incorporation level was increased at the same time, reaching 39.5% mol. At a lower Al:Zr molar ratio of 25:1, both the drop in the catalyst activity and the increase in the 1-octene incorporation level were smaller (run 6, 18.3 mol%), while the increase in the Al:Zr ratio to 150:1 resulted in even greater incorporation of the comonomer (run 5, 64.6 mol%). The use of AlEt<sub>3</sub> and Al*i*Bu<sub>3</sub> (runs 4 and 7, respectively) did not cause such changes as the addition of AlMe<sub>3</sub>; the catalyst activity remained nearly the same as in run 2, and the comonomer incorporation level also turned out to be comparable (8.1 and 10.6 mol%, respectively).

It is well known that the use of a simple alkylaluminum compound in conjunction with an activator may influence the activity of metallocene catalysts in olefin (co)polymerization [23] and the kinetics of ethylene polymerization [24]. AlMe<sub>3</sub> is known to be able to form different kinds of complexes with the metallocene catalysts, some of which are inactive in olefin polymerization [14, 25]. No activity or low activity, probably due to stability of [LZr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> and [LZr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>, was observed for the catalytic system consisting of the metallocene complex, AlMe<sub>3</sub> and Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as a cation forming reagent [26]. The strong bonding of AlMe<sub>3</sub> species to the metal cation decreased the polymerization activity of the hafnocene catalyst in 1-hexene polymerization as well [23]. However, it has been reported that the intermediate [(Cp-R)<sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[counteranion]<sup>-</sup> (R = *n*Bu, *t*Bu, 1,2,3-Me<sub>3</sub>) is the actual precursor of the active centers in ethylene polymerization [25]. Similarly, the activation of bis[N-(3-*tert*-butylsalicylidene)anilinato] zirconium(IV) dichloride with MAO and AlMe<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> led to the heterobinuclear ion pairs [(L<sup>*t*Bu</sup>)<sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> or [(L<sup>*t*Bu</sup>)<sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[Me-MAO]<sup>-</sup>, which are precursors of highly active intermediates in polymerization. However, in the case of the ligand with a smaller substituent on the phenolate ring (Me), a tight ion pair was formed with low activity in polymerization [27]. Previously, the formation of cationic active species was observed for the catalyst based on [LigZrCl]<sub>2</sub>(μ-O) [20], and therefore, we could suppose that the inhibitory effect of AlMe<sub>3</sub> resulted from its interaction with the cationic zirconium active site by forming heterobinuclear cations that were highly stable. To confirm those suppositions, the complex [LigZrCl]<sub>2</sub>(μ-O) was activated with AlMe<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> instead of Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>. The [LigZrCl]<sub>2</sub>(μ-O)/AlMe<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> system with the Zr:Al:B molar ratio of 1:15:1.5 produced traces of copolymer only. The tests showed that there was also no catalytic activity when copolymerization was carried out in the presence of an additional amount of AlMe<sub>3</sub> (the same process conditions

and concentrations of reacting substances were adopted as in run 3). These results correlate with the observed decrease in the activity of the [LigZrCl]<sub>2</sub>(μ-O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> catalytic system after addition of AlMe<sub>3</sub> to the polymerization feed. Despite the strong interaction of AlMe<sub>3</sub> with the zirconium cation, which leads to low overall activity, the catalyst inhibition does not take place when other organoaluminum compounds are employed; they probably do not form such adducts, or those adducts are less stable.

The obtained copolymers were further characterized by GPC. The molecular weight of the copolymer 2 (synthesized without any additional alkylaluminum) was higher than the molecular weight of the copolymers synthesized with AlR<sub>3</sub> (runs 3, 4, and 7). Hence, the organoaluminum compounds in each case take part in the chain transfer reaction, which yields low molecular weight products. Migration of the polymeryl group from the active site to Al is one of the common chain transfer reactions that can be used to tune the molecular weight and end group(s) of the olefin polymers [28]. The performance of the compounds in question in that reaction changes as follows: AlEt<sub>3</sub> > Al*i*Bu<sub>3</sub> > AlMe<sub>3</sub>. Previous studies of propylene and ethylene polymerizations have also shown that the chain transfer to AlEt<sub>3</sub> occurred more frequently than that to Al*i*Bu<sub>3</sub> [15, 26]. The GPC analysis of copolymers demonstrated that their molecular weights decreased with the increasing concentration of the aluminum compound (runs 3 and 5, Table 1). Moreover, as shown in Fig. 2a, the copolymers produced with the use of AlR<sub>3</sub> are characterized by a higher dispersity than copolymer 2. The use of AlMe<sub>3</sub> (run 3) gives a copolymer with a bimodal distribution of its molecular weights. This polymer contains an additional fraction with a high molecular weight, which is close to that of the copolymer obtained with no AlMe<sub>3</sub>. That fraction disappears when the molar ratio is increased to 150:1 (Fig. 2b).

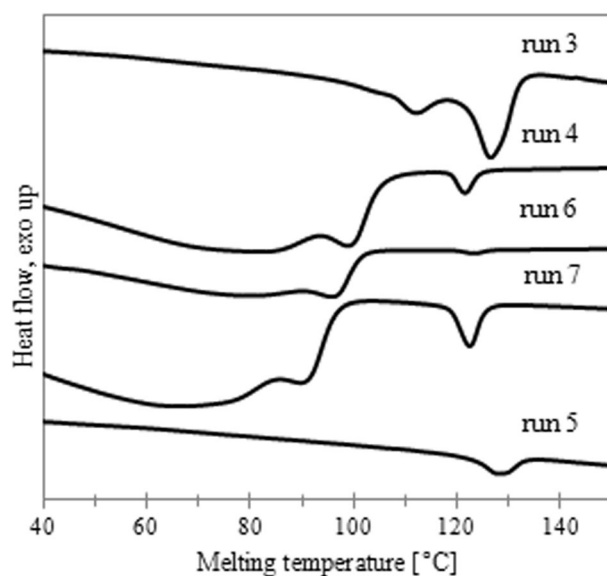
The ethylene/1-octene copolymer obtained without the use of AlMe<sub>3</sub> is characterized by a very wide melting range, from ~25 to 115 °C. The DSC analysis of the copolymer produced in run 3 (Fig. 3) showed two melting peaks, with melting points at 126.3 and 111.9 °C, corresponding to the copolymer fractions with low and medium incorporation (based on the equation presented in [29], the content of short chain branching in these fractions amounts to ~3.5 and 9.9 CH<sub>3</sub>/1000 C). The DSC curves for the copolymers obtained at the same reaction conditions but with other alkylaluminum compounds, AlEt<sub>3</sub> and Al*i*Bu<sub>3</sub>, showed broad melting peaks in the low temperature range and small melting peaks at ~122 °C (Fig. 3). When the AlMe<sub>3</sub>:Zr molar ratio was increased from 100:1 to 150:1, the 1-octene incorporation level was further increased, reaching 64.6 mol %, and as can be deduced from its DSC curve, this product



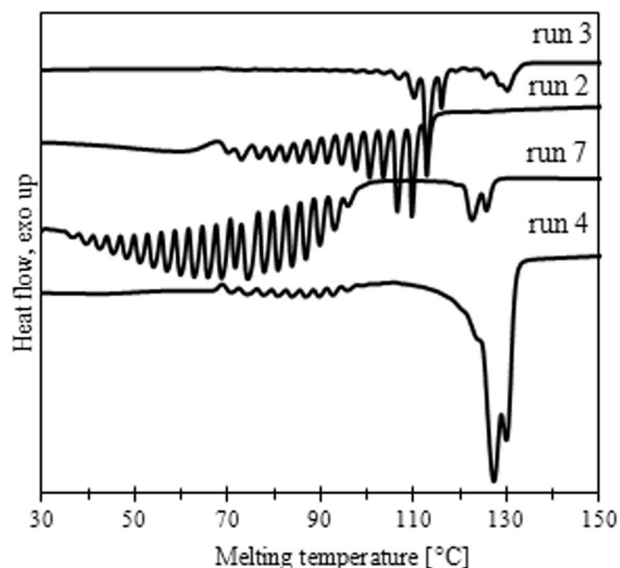
**Fig. 2** Molecular weight distributions of the ethylene/1-octene copolymers: **a** effect of  $\text{AlR}_3$  addition (runs 2–4) and **b** effect of the  $\text{AlMe}_3$ :Zr molar ratio (runs 3 and 5)

contained only small amounts of crystalline material with a melting point at 127.8 °C.

More information about the distribution of the comonomer along the copolymer chains can be obtained by thermal fractionation. Thus, copolymers 2, 3, 4, and 7 were subjected to the successive self-nucleation and annealing (SSA) treatment, as this method is the most convenient technique used for that purpose [29]. The SSA treatment consisted of 25 steps with  $T_s$  temperatures within the range of 140–68 °C for copolymers 2, 3, and 4; whereas, the temperature range for copolymer 7 was widened to 140–32 °C due to the shift in the melting range to lower temperatures. The obtained thermograms are presented in Fig. 4. The scope of the temperatures at which the fifteen melting peaks appear is very broad for copolymer 2, from ~70 to 113 °C, and the distribution of the melting points is multimodal, which indicates the heterogeneous nature of that copolymer. Regarding copolymer 3, obtained after addition of  $\text{AlMe}_3$ ,



**Fig. 3** Melting curves of ethylene/1-octene copolymers synthesized with zirconium catalyst without and with  $\text{AlR}_3$



**Fig. 4** DSC heating scans of ethylene/1-octene copolymers synthesized with zirconium catalyst without (run 2) and with the presence of  $\text{AlR}_3$  (R = Me, run 3; R = Et, run 4; R = *i*Bu, run 7) obtained after SSA thermal treatment

the short chain branching distribution (SCB) is bimodal, and the melting peaks are shifted toward higher values (they appeared in the range of 100–131 °C). This finding suggested the presence of less branched and longer, uninterrupted linear chain sequences. However, this result can be misleading because the DSC analysis perceives only the crystalline fraction in the copolymers and neglects the presence of highly branched structures that form the amorphous material. The high comonomer incorporation level indicates that this copolymer contains a substantial

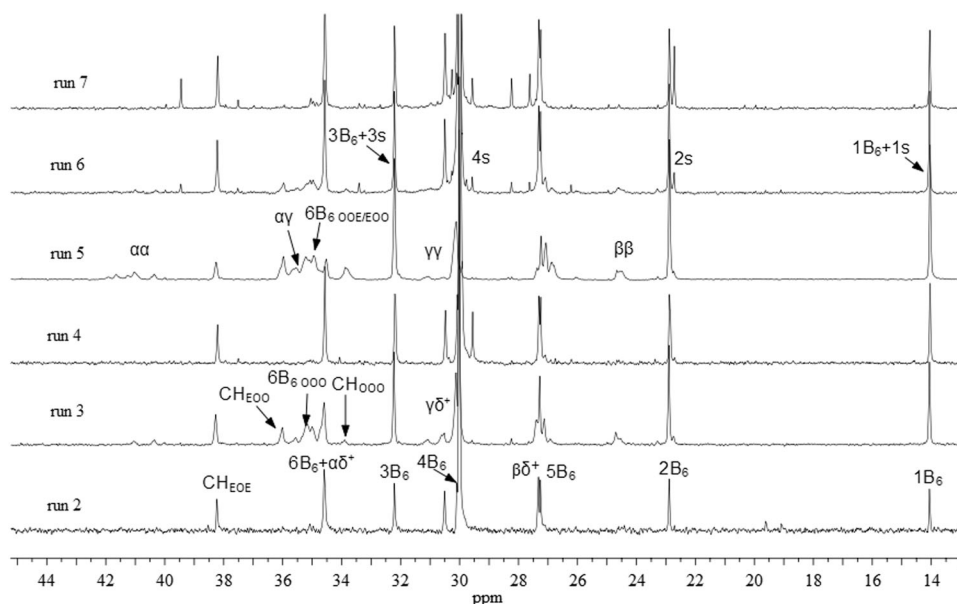
amount of the highly branched non-crystallizing fraction. The DSC heating scan of the copolymer obtained with the use of  $\text{Al}i\text{Bu}_3$  also revealed the presence of highly linear fractions of the copolymer having  $T_m$  equal to 123 and 126 °C. Their contribution, however, is small, and the branched fractions with  $T_m$  in the range of 36–96 °C clearly predominate. The thermal fractionation of copolymer 4, which was synthesized in the presence of  $\text{AlEt}_3$ , results in a very similar distribution of melting points. There are two clearly separated groups of macromolecules in the copolymer: the fractions that contain macromolecules with long crystallizable chain segments, with  $T_m$  close to  $T_m$  of the ethylene homopolymer (~130 °C), and the fractions that have highly branched sequences, with  $T_m$  within 68–100 °C. Chemical non-uniformity of the copolymers can result from both the significant changes in the comonomer ratio in the feed during the copolymerization (high conversion of 1-octene leads to the production of more linear macromolecules with high  $T_m$ ) and the presence of different active sites in zirconium catalysts [19].

The results of ethylene/1-hexene copolymerization carried out with the zirconium catalyst in the absence and with the addition of  $\text{AlR}_3$  are included in Table 1 (runs 8–10 A). The changes in the catalytic activity and in the properties of ethylene/1-hexene copolymers after introduction of  $\text{AlMe}_3$  were very comparable to those obtained for ethylene/1-octene copolymerization, e.g., the catalytic activity and the molecular weight significantly decreased. Moreover, as determined by  $^{13}\text{C}$  NMR spectroscopy, the 1-hexene incorporation level increases from ~7.9 mol% to 30.5 mol% after  $\text{AlMe}_3$  is added. In turn,  $\text{AlEt}_3$  and  $\text{Al}i\text{Bu}_3$  are effective chain termination agents, but they affect the polymer yield and the comonomer content (10.0 and 7.4 mol%) to a much lower degree.

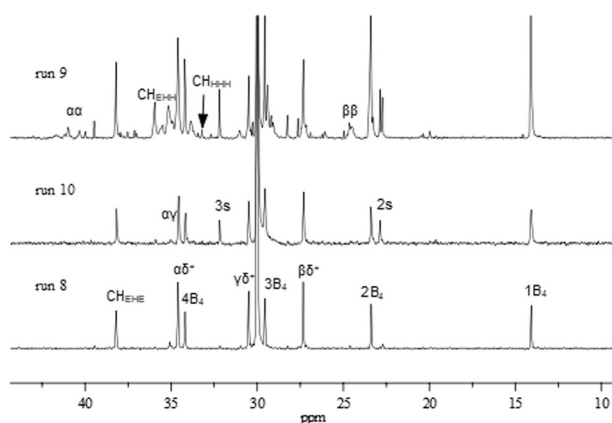
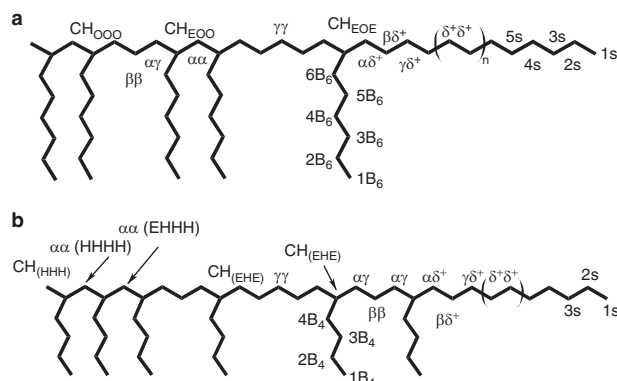
The microstructure of the synthesized copolymers was studied by  $^{13}\text{C}$ -NMR spectroscopy. The spectra of poly(ethylene-co-1-octene) are given in Fig. 5. The nomenclature system used (Fig. 6) and chemical shift assignments are the same as reported in [30, 31]. However, the 100.6 MHz  $^{13}\text{C}$  NMR spectra obtained in this study failed to show all the signals observed in the 188.6 MHz  $^{13}\text{C}$  NMR spectra [30] because of the lower resolution. As seen, the spectrum of the copolymer obtained in run 2 shows resonances at 14.06 ( $1\text{B}_6$ ), 22.88 ( $2\text{B}_6$ ), 27.26 ( $5\text{B}_6$ ), 27.33 ( $\beta\delta^+$ ), 30.00 ( $\delta^+\delta^+$ , EEE), 30.09 ( $4\text{B}_6$ ), 30.50 ( $\gamma\delta^+$ ), 32.21 ( $3\text{B}_6$ ), 34.59 ( $\alpha\delta + /6\text{B}_6$ ), and 38.22 ppm (CH, EOE). Accordingly, only isolated 1-octene units are present in this copolymer. The identical signals appear in the spectrum of copolymer 4, obtained with the use of  $\text{AlEt}_3$ , and copolymer 7, produced in the presence of  $\text{Al}i\text{Bu}_3$ . Additionally, due to the low molecular weight of those polymers, weaker signals appear at 22.87, 29.57, 29.92, and 32.18 ppm, which can be attributed to the 2 s, 4 s, 5 s, and 3 s carbons at the saturated end of the main chain, respectively. The main chain end resonance from the 1 s carbon cannot be observed in the spectrum because it is obscured by the  $1\text{B}_6$  resonance.

The spectrum of the sample obtained from copolymer 3, synthesized with  $\text{AlMe}_3$  at the same Al:Zr molar ratio, appears different. In addition to the signals observed in the spectrum of copolymer 2 resulting from the presence of the isolated 1-octene units and signals of saturated chain end carbons (due to lower molecular weight), the signals at 41.04, 40.33, and 39.99 ppm, arising from  $\alpha\alpha$  carbons, and the signals at 36.00 and 33.89 ppm, ascribed to the methine carbons from OOE/EOO and OOO triads, could be observed, indicating the presence of contiguous sequences of 1-octene units. The new resonances within 34.95–35.56

**Fig. 5**  $^{13}\text{C}$ -NMR spectra of ethylene/1-octene copolymers obtained in runs 2–7



**Fig. 6** General structure of poly(ethylene-co-1-octene) (a) and poly(ethylene-co-1-hexene) (b)



**Fig. 7** <sup>13</sup>C-NMR spectra of ethylene/1-hexene copolymers obtained in runs 8–10

ppm can be assigned to  $\alpha\gamma$  and  $6B_6$  carbons. There are also clear signals in the spectrum at 31.05 ppm that arise from the  $\gamma\gamma$  methylene carbons, the signals at 24.52, 24.58, and 24.69 ppm arise from the  $\beta\beta$  methylene carbons from the EOEOE, OOEOE, and OOEOO joints, and a new peak ~27 ppm is due to the  $5B_6$  carbon in the sequences OOE/EOO and OOO. The spectrum of copolymer 5, where more AlMe<sub>3</sub> was used, is very similar to that for copolymer 3, while the intensities of resonances are different. First, the  $\delta^+\delta^+$  signal of methylene carbons was less intense, and the intensity of the resonances associated with the sequences of successive octene units increased. The spectrum of copolymer 6, obtained at Al:Zr = 25:1, also shows the signals mentioned above, but they are much less intense.

When AlEt<sub>3</sub> and AlMe<sub>3</sub> were added to the reaction medium, they resulted in analogous microstructural changes in the copolymer of ethylene and 1-hexene. As shown in Fig. 7, the spectrum of poly(ethylene-co-1-hexene) produced by the catalytic system [LigZrCl]<sub>2</sub>( $\mu$ -O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> shows only the signals from the joint EHE, EEH,

and EEE (chemical shift assignments for ethylene/1-hexene copolymers based on [32, 33] and the nomenclature system are presented in Fig. 6). The presence of AlEt<sub>3</sub> has no effect on the copolymer microstructure (run 10 in Fig. 7), but because it is a low molecular weight polymer, the clear signals of the 3 s, 2 s, and 1 s carbons from the *n*-alkyl chain end, at 32.19, 22.87 and 14.05 ppm (this peak overlaps with the 1B<sub>4</sub> signal), are also present. In the copolymer 9 spectrum, which was produced with the same catalytic system after addition of AlMe<sub>3</sub> instead of AlEt<sub>3</sub>, the signals at 41.40, 40.86, and 40.18 ppm arising from  $\alpha\alpha$  carbons can be observed in addition to the signals mentioned above, indicating the presence of contiguous 1-hexene units in the copolymer chains. CH carbons from the sequences EHE, EHH, and HHH give resonances at 38.20, 35.96, and 33.86 ppm, respectively. In turn, the resonances at 24.65–24.36 ppm are attributed to the  $\beta\beta$  carbon. There are small additional peaks in the spectrum that probably originate from regio-irregular linkages between consecutive 1-hexene units.

Thus, only when AlMe<sub>3</sub> is added to the ethylene/1-olefin copolymerization catalyzed by [LigZrCl]<sub>2</sub>( $\mu$ -O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> is a spectacular change in copolymerization ability observed. The amount of incorporated comonomer is increased a few times, and it goes up with the increasing content of organoaluminum compound in the reaction medium. To the best of our knowledge, such a spectacular switch in incorporation ability is unprecedented. Some small change in comonomer incorporation (from 8 wt% to 11 wt%) was previously noted, when the effect of Al*i*Bu<sub>3</sub> on the yield of the copolymerization process catalyzed by Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO and conducted in an aliphatic solvent was studied [34]. The mechanism of these changes is not currently clear. The chain transfer from the catalytically active site to the alkylaluminum can be reversible in some cases. Thus, alkylaluminum compounds can be used as CTAs in CCTcoP. In the case of CCTcoP of olefins, the change in the amount of added CTA had no significant effect on the

**Table 2** Effect of AlR<sub>3</sub> on ethylene/1-olefin copolymerization catalyzed by various catalytic systems

Run	Complex	1-olefin	AlR <sub>3</sub> :Zr [mol/mol]	Yield [g]	Activity [kg/(mol <sub>Zr</sub> ·h)]	M <sub>w</sub> [g/mol]	Đ	[O] (or [H]) [mol%]
11 <sup>a</sup>	(Lig <sup>FI</sup> ) <sub>2</sub> ZrCl <sub>2</sub>	1-hexene	—	1.845	147.6	nd	nd	2.6
12 <sup>a</sup>	(Lig <sup>FI</sup> ) <sub>2</sub> ZrCl <sub>2</sub>	1-hexene	100/1	0.302	24.2	nd	nd	7.6
13 <sup>b</sup>	Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	1-octene	—	0.505	1442.9	53000	2.8	2.5
14 <sup>b</sup>	Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>	1-octene	100/1	0.138	394.3	38000	3.9	4.0
15 <sup>c</sup>	LigTiCl <sub>2</sub>	—	—	1.439	57.6	nd	nd	—
16 <sup>c</sup>	LigTiCl <sub>2</sub>	1-octene	—	1.542	61.7	131200	1.3	4.0
17 <sup>c</sup>	LigTiCl <sub>2</sub>	1-octene	100:1	0.628	25.1	57500	1.4	4.7
18 <sup>c,d</sup>	LigTiCl <sub>2</sub>	1-octene	100:1	1.011	40.4	42900	2.0	5.0
19 <sup>c</sup>	LigTiCl <sub>2</sub>	1-octene	150:1	0.228	9.1	54900	1.4	nd

nd not determined

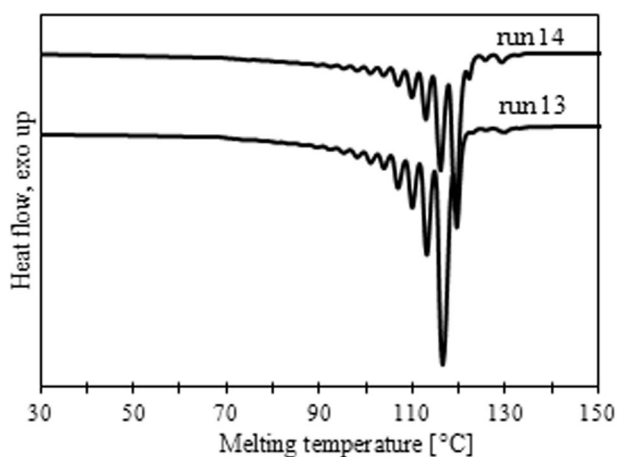
Copolymerization conditions: <sup>a</sup>0.025 mmol of (Lig<sup>FI</sup>)<sub>2</sub>ZrCl<sub>2</sub>, 0.038 mmol of Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, 0.375 mmol of Al*i*Bu<sub>3</sub>, AlR<sub>3</sub> = AlMe<sub>3</sub>, 30 min, 5 bar of ethylene, 5 mL of 1-hexene, 60 °C; <sup>b</sup>0.7 μmol of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, 5.0 mmol of MMAO, AlR<sub>3</sub> = AlMe<sub>3</sub>, 50 °C, 30 min, 100 mL of toluene, 5 bar of ethylene, 5 mL of 1-octene; <sup>c</sup>0.050 mmol of LigTiCl<sub>2</sub>, 0.075 mmol of Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, 0.75 mmol of Al*i*Bu<sub>3</sub>, AlR<sub>3</sub> = AlMe<sub>3</sub>, 60 °C, 30 min, 5 bar of ethylene, 5 mL of 1-octene; <sup>d</sup>AlR<sub>3</sub> = AlEt<sub>3</sub>

composition of the copolymer product (the differences were within 2–3 mol%) [10, 13], which results from the mechanism of that reaction. The reversible chain transfer should generate polymers with a narrow molecular weight distribution, whereas a simple chain transfer broadens it [13]. The increased dispersion of copolymers after the use of AlMe<sub>3</sub> was observed in our research. On the other hand, CTA should not affect the comonomer incorporation level: after the polymer chain is transferred to Al, a dormant species is formed, and the macromolecule can further grow only after the chain is transferred again to the transition metal. Hence, it seems more likely that AlMe<sub>3</sub> interacts with the active site to modify its catalytic properties, and the higher 1-olefin is incorporated preferentially as a result. Thus, the modified composition of the ethylene/1-olefin copolymer in the presence of AlMe<sub>3</sub> can also indicate an easier displacement of AlMe<sub>3</sub> from its adduct with the alkyl zirconium cation by 1-octene than by ethylene. In turn, AlEt<sub>3</sub> and Al*i*Bu<sub>3</sub> do not affect comonomer reactivity and catalyst activity, and hence, they do not change the nature of active sites. Furthermore, the microstructure of the copolymers produced is dependent on the presence of AlMe<sub>3</sub>. With AlMe<sub>3</sub>, copolymers are formed that contain longer sequences of higher 1-olefin units. However, that may result only from a much higher comonomer incorporation, reaching 64.6 mol%.

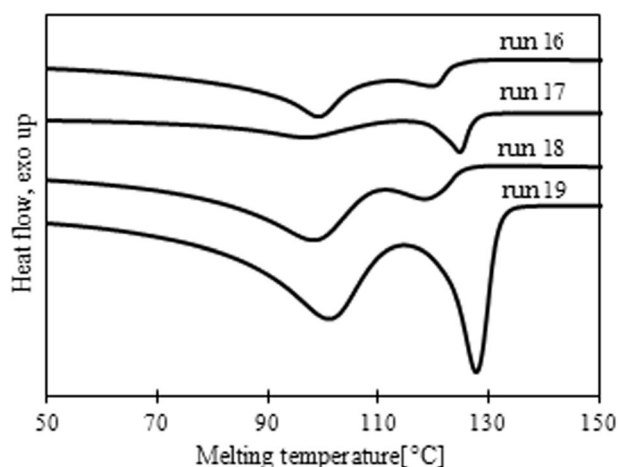
To check whether the observed effect of AlMe<sub>3</sub> on the copolymer composition and microstructure is a specific feature of [LigZrCl]<sub>2</sub>(μ-O)/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> or a more general attribute of the zirconium catalysts, the effect of

alkylaluminum addition on the catalytic properties of two other zirconium catalysts was evaluated. The ethylene/1-hexene copolymerization process was carried out with the bis(phenoxy-imine) catalyst, (Lig<sup>FI</sup>)<sub>2</sub>ZrCl<sub>2</sub>/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (where Lig<sup>FI</sup> = (C<sub>6</sub>H<sub>5</sub>)N = CH(2-O-3,5-*t*Bu<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>)), and the ethylene/1-octene copolymerization reaction was catalyzed by Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MMAO. In each case, 5 mL of the comonomer was added to the polymerization, and the molar ratio AlMe<sub>3</sub>:Zr = 100:1 was maintained in the polymerization processes. The results, included in Table 2, showed that ethylene/1-hexene copolymer produced by (Lig<sup>FI</sup>)<sub>2</sub>ZrCl<sub>2</sub>/Al*i*Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (run 11) was characterized by a somewhat low level of the built-in comonomer (2.6 mol%). After the use of AlMe<sub>3</sub> (run 12), the catalytic activity was poorer, and the 1-hexene incorporation significantly increased, to 7.6 mol%. The <sup>13</sup>C NMR spectrum of copolymer 11 (Fig. S1), which was obtained without the use of AlMe<sub>3</sub>, revealed only isolated 1-hexene units between polyethylene blocks, while additional resonances appeared in the spectrum of copolymer 12, which contained more 1-hexene. The signals at 30.9 ppm and at 24.60 ppm were due to the γγ carbon in the sequence HEEH (1,7-dibutyl branched) and ββ carbon in the sequence EHEHE, the resonance at 35.06 ppm was due to the sequences HEHE (1,5-dibutyl branches), and the CH carbon from the sequence EHH gives a signal at 35.93 ppm. The copolymer produced by Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MMAO in the presence of additional AlMe<sub>3</sub> had a lower molecular weight and broader dispersity (run 14) than the copolymer synthesized without alkylaluminum (run 13), but the

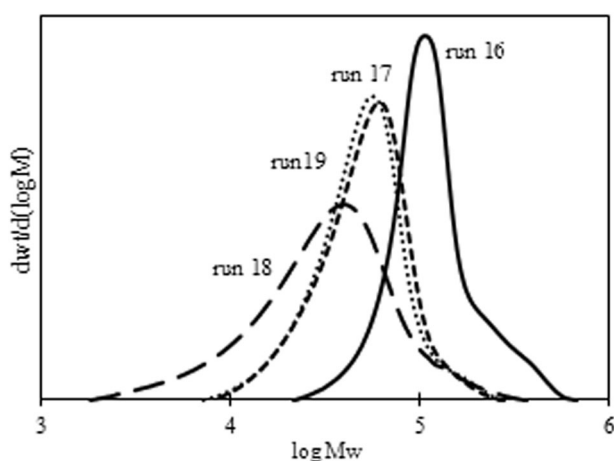




**Fig. 8** DSC endotherms of ethylene/1-octene copolymers synthesized with  $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MMAO}$  without and with the presence of  $\text{AlMe}_3$  obtained after SSA treatment



**Fig. 10** Melting curves of ethylene/1-octene copolymers synthesized with titanium catalyst without and with  $\text{AlR}_3$  (R = Me, Et)



**Fig. 9** GPC results for ethylene/1-octene copolymers synthesized with titanium catalyst without and with  $\text{AlR}_3$  (R = Me, Et)

comonomer incorporation levels and heterogeneity, as shown by thermal fractionations (Figs. S2-S3, Fig. 8) of both those copolymers, were quite similar.

### Effect of $\text{AlR}_3$ on catalytic properties of $\text{LigTiCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$

The contribution of an organoaluminum compound to the course of the ethylene/1-octene copolymerization reaction was also studied for the catalytic system containing a diamino-bis(phenolate) titanium complex (Fig. 1) instead of the zirconium one, i.e.,  $\text{LigTiCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ . As for the zirconium catalyst, all copolymerization tests involved 5 ml of comonomer (0.27 mol/L) and were run at 60 °C, over 30 min, at 5 bar of ethylene (Table 2). That catalyst produced poly(ethylene-co-1-octene) with a high molecular weight (131,000 g/mol), narrow molecular-

weight distribution (Fig. 9) and comonomer incorporation level equal to 4 mol%. The DSC analysis shows that the copolymer contains two fractions of macromolecules with different comonomer incorporation levels, with melting points of 99.0 and 115.0 °C (Fig. 10). The use of an organoaluminum compound at the molar ratio to the complex of 100:1, regardless of whether  $\text{AlMe}_3$  or  $\text{AlEt}_3$ , lowers the catalytic activity, with much more detrimental performance from  $\text{AlMe}_3$ . The use of an organoaluminum compound also resulted in the lowered molecular weight of the copolymer, slightly increased dispersity (Table 2, Fig. 9) and only slightly increased the comonomer incorporation level ( $\leq 1$  mol%). The microstructures of the obtained copolymers, however, were not affected (Fig. S4). Additionally, no changes in the thermogram profiles were observed (Fig. 10), and the minima of endothermic peaks were slightly shifted towards lower and higher temperatures when  $\text{AlMe}_3$  was used.<sup>3</sup>

## Conclusions

Until now, no studies have been conducted on the effects of alkylaluminum addition to catalytic systems on the comonomer incorporation levels and microstructures of ethylene/1-olefin copolymers. The results presented showed that addition of  $\text{AlR}_3$  to homogeneous catalysts, which contain transition metal complexes with multi-donor ligands, may significantly affect the catalytic properties of the system. This influence is dependent on the type of organoaluminum compound and on the structure of the complex, i.e., on the structure of the ligand and on the type of transition metal. It was shown that the presence of additional  $\text{AlR}_3$  always decreases the molecular weight. Furthermore, addition of  $\text{AlMe}_3$  induced changes in the composition

and microstructure of the copolymers produced by the zirconium complexes with O,N-bidentate or O,N,N',O-tetradentate ligands. To the best of our knowledge, such a spectacular switch in the incorporation ability, as in the case of the ethylene/1-olefin copolymerization catalyzed by  $[\text{LigZrCl}_2(\mu\text{-O})/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4]$  (from approximately 10 to approximately 65 mol%), is unprecedented.  $\text{AlMe}_3$  enhanced the 1-olefin incorporation level, although that was less significant, also in the case of the copolymerization reaction catalyzed by another zirconium catalyst,  $(\text{Lig}^{\text{Fl}})_2\text{ZrCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ , but such an effect was not observed for the titanium catalyst,  $\text{Lig-TiCl}_2/\text{Al}i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ . The use of other organoaluminum compounds as additional components of the catalytic systems did not significantly affect the copolymer compositions.

### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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