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Studies of structural composition distribution heterogeneity in ethylene/1-hexene copolymers using thermal fractionation technique (SSA)
Effect of catalyst structure

Marzena Białek*, Krystyna Czaja, Beata Sacher-Majewska

Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

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Abstract

Investigations into the compositional heterogeneity of ethylene/1-hexene copolymers obtained with various zirconocene/MAO catalysts, either homogeneous or supported on inorganic carriers such as a complex of magnesium chloride with tetrahydrofuran or methyl alcohol, were conducted. The dependence between metallocene structure, as well as catalyst immobilization, and the compositional heterogeneity of the related products was investigated. It was found that the heterogeneity of copolymers is determined by the metallocene catalyst structure. The amount of peaks on the DSC thermograms of copolymers and their division increase with the increase of bulkiness of the ligand in the catalytic system. The immobilization of the investigated catalysts on the magnesium carrier leads to an increase of the copolymer's compositional heterogeneity. However, the modification of the $MgCl_2$ carrier by tetrahydrofuran or methyl alcohol seems to not have any influence on the copolymers' CCD.

Keywords: Metallocene catalyst; Structure; Support; Copolymers; Compositional heterogeneity

1. Introduction

Linear low-density polyethylenes (LLDPEs) that are obtained by the copolymerization of ethylene with a small amount of higher olefin such as 1-butene, 1-hexene or 1-octene, are, at present, one of the most important classes of synthetic polymers. Incorporation of the other olefin molecule into a polyethylene chain results in the final stage in polymeric materials with favoured properties that cannot be achieved through ethylene homopolymerization.

This type of copolymer, like other synthetic copolymers, is heterogeneous with relation to both molecular weight and structural composition. The difference in the size of the macromolecules is characterized by molecular weight distribution (MWD, $\overline{M}_w/\overline{M}_n$). In the case of copolymer composition, the macromolecules can differ in the amount of comonomer incorporated as well as comonomer distribution along the copolymer chain (chemical composition distribution—CCD). As the physical properties of these copolymers, and, eventually, polymer behaviour during processing in addition to its final operational properties, are dependent on the above-mentioned quantity, it is necessary to know the value of all the above named quantities and establish the structure–property–processing relationship [1].

Recently, to characterize compositional heterogeneity of copolymers three main methods have been used: temperature rising elution fractionation (TREF) [2–8], crystallization analysis fractionation (CRYSTAF) [6,9] and DSC fractionation techniques [2,3,6,10–18]. The last method includes many techniques such as the stepwise isothermal segregation technique (SIST), stepwise crystallization (SC) or successive self-

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* Corresponding author.
E-mail addresses: marzena.bialek@uni.opole.pl (M. Białek), krystyna.czaja@uni.opole.pl (K. Czaja), bsacher@uni.opole.pl (B. Sacher-Majewska).

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nucleation/annealing (SSA). All these DSC techniques are based on the special heat treatment of samples and the subsequent analysis of melting behaviour by DSC [12]. Comparative studies of the mentioned methods have been made. It was shown that the DSC methods are not only less time consuming in comparison to TREF but also give comparable results [6]. It seems that among them SSA is the most promising; it exhibits better separation than SC, especially in the low temperature region, and provides results in a shorter time [14]. Our previous study confirmed this observation [17]. Therefore, in the present work the SSA procedure was chosen for the investigation of the heterogeneity of ethylene/1-hexene copolymers.

The structural and molecular parameters of ethylene/1-olefin copolymers are strictly related to the catalyst type used for copolymerization and the copolymerization conditions [13]. Many metallocene catalysts provide polyethylenes with narrow molecular weight distribution and it is believed that they should produce ethylene/1-olefin copolymers with narrow comonomer compositional distribution. Such an ability by these catalysts differentiates them from traditional titanium or vanadium-based Ziegler–Natta ones, which produce polymers with broad MWD and CCD [3,15]. In our previous study [17], the influence of catalyst type metallocene and Ziegler–Natta (bis(cyclopentadienyl)zirconocene dichloride and vanadium oxytrichloride catalysts supported on an inorganic support), on the intermolecular heterogeneity of ethylene/1-hexene copolymers was investigated. It was found that copolymer obtained by supported metallocene catalyst is not homogeneous with regards to its composition. However, it is less heterogeneous than a Ziegler–Natta based one. In this paper, those investigations are extended to copolymers obtained by different zirconocene/MAO catalysts: either homogeneous ones or supported on inorganic carriers such as a complex of magnesium chloride with tetrahydrofuran or methyl alcohol. The dependence between the metallocene structure and the structure of the related products, as well as the influence of catalyst immobilization on copolymer compositional heterogeneity is presented.

2. Experimental

2.1. Materials and synthesis process

The ethylene/1-hexene copolymers were synthesised by a metallocene catalyst either homogeneous or supported on inorganic supports: a complex of magnesium chloride with tetrahydrofuran or methyl alcohol. The magnesium carriers were chemically modified before their use (treated with $Al(i\text{-}Bu)_3$). The metallocene precursors were heterogenized on the support surface by ball-milling the catalyst component in toluene. Then the solid product was filtered off, washed four times with hexane and dried. For copolymerization, supported catalysts were used as a suspension in hexane (the homogeneous ones were only dissolved in toluene). The copolymerization processes were carried out in an aliphatic solvent (hexane), at 50 °C, at constant ethylene pressure (0.5 MPa) for 30 min. As a cocatalyst methylaluminoxane (MAO) was used.

2.2. Methods

The 1-hexene content was determined by ^{13}C NMR and FT-IR spectroscopy according to the procedures described in Refs. [19–21]. The molecular weight and molecular weight distribution of the copolymer was estimated by gel permeation chromatography (GPC) [19].

Differential scanning calorimetry (DSC) measurements were performed using the apparatus DSC-2010 TA Instruments. The melting temperature and heat of fusion (ΔH) determinations were obtained from samples formerly melted and recrystallized, which then were heated to 180 °C at the rate 10 °C/min. From the ΔH the percentage of crystallinity was calculated using the expression: $C\ (\%) = \Delta H(100/290)$ [22]. The SSA fractionation was performed according to the principles described earlier [17]. Initially, the samples were heated to 170 °C at the rate 10 °C/min and maintained at this temperature for 5 min. Then the samples were cooled to 0 °C. Heating–annealing–cooling cycles were repeated for temperatures: 125, 119, 114, 111, 107 and 103 °C. The figures are presented in original form generated by TA-Instruments DSC 2010 software package. For determination of single peak areas of overlapping DSC peaks, Netzsch Peak Separation software was used. The peak profile was simulated by asymmetrical Fraser–Suzuki function.

3. Results and discussion

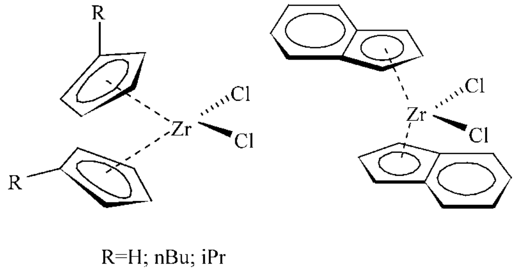
Much research carried out nowadays deals with the polymerization and copolymerization of olefin with metallocene catalysts. Most of them refer to the influence of catalyst structure on catalyst activity; comonomer incorporation; and the molecular weight of (co)polymer and its distribution. The other problem often investigated is heterogenization of catalytic systems and its influence on polymer yields and properties. In our study, the impact of catalyst structure and catalyst heterogenization on ethylene/1-hexene compositional heterogeneity was investigated. The structures of the studied zirconocene compound are presented in Scheme 1.

As can be seen, the zirconocene compounds differ in type of ligand L_2ZrCl_2 (L = cyklopentadienyl or indenyl) and in the case of Cp_2ZrCl_2, the ligand Cp can contain substituent R (R = *iso*-propyl or *n*-butyl). In order to examine the effect of catalyst heterogenization on polymer structures some of these compounds were immobilized on an inorganic carrier (a complex of magnesium chloride with tetrahydrofurane or methyl alcohol). The basic characteristics of ethylene/1-hexene copolymers obtained with the above-mentioned catalysts are listed in Table 1.

Table 1
Properties of ethylene/1-hexene copolymers studied

Catalyst composition[a]	1-Hexene content (mol%)	Molecular weight ($\times10^{-3}$) ($\overline{M}_w$)	$\overline{M}_w/\overline{M}_n$	Melting temperature (°C)	Crystallinity (%)
Cp_2ZrCl_2	6.4	6.3	3.4	110.6	39.1
$(i\text{PrCp})_2ZrCl_2$	6.9	15.8	3.0	111.9	41.3
Ind_2ZrCl_2	6.7	78.1	3.8	110.3	30.3
$MgCl_2(THF)_2/Al(i\text{-Bu})_3/Cp_2ZrCl_2$	6.7	17.1	1.8	119.2	35.3
$MgCl_2(MeOH)_4/Al(i\text{-Bu})_3/Cp_2ZrCl_2$	6.3	14.1	2.5	119.1	47.0
$(n\text{BuCp})_2ZrCl_2$	4.9	17.6	3.3	112.5	49.2
$MgCl_2(THF)_2/Al(i\text{-Bu})_3/(n\text{BuCp})_2ZrCl_2$	4.6	89.7	3.1	113.9	40.5

[a] Cocatalyst: MAO.



Scheme 1. Structures of metallocene compounds used for ethylene/1-hexene copolymers synthesis.

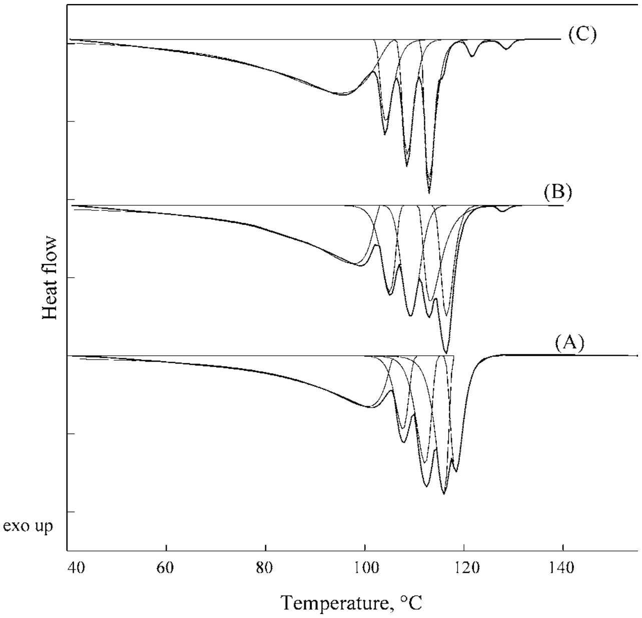


Fig. 1. Comparison of the melting curves of ethylene/1-hexene copolymers obtained with Cp_2ZrCl_2/MAO (A), $(i\text{PrCp})_2ZrCl_2$/MAO (B) and Ind_2ZrCl_2/MAO (C) catalysts using the SSA method for analysis.

It is known that, during conventional DSC heating of ethylene/1-olefin copolymers, the increase of 1-olefin contribution in copolymer cause the DSC peak widening, and in some cases even two melting peaks appear [17]. On the conventional DSC curves of copolymers investigated by us only peak broadening was observed. The DSC endotherms of the copolymers synthesised with homogeneous metallocene catalytic systems Cp_2ZrCl_2/MAO (A), $(i\text{PrCp})_2ZrCl_2$/MAO (B), Ind_2ZrCl_2/MAO (C) after thermal fractionation using the SSA method are presented in Fig. 1. All copolymers contain a similar amount of 1-hexene incorporated (about 6.4–6.9 mol.%) and have similar polydispersity ($\overline{M}_w/\overline{M}_n$ = 3.0–3.8) but very different molecular weights (from 6.3×10^3 to 78.1×10^3). During the isothermal crystallization steps the separation of the crystalline material into groups of lamellae of different thicknesses, depending on the amount and distribution of the 1-olefin units in the macromolecular chain, take place [13]. In other words, on the DSC thermogram, after thermal fractionation endotherms appeared, each one representing molecules with different branches content. The short branches reduce the regularity of the polymer chains and decrease the lamellar thickness of the formed crystallites. The greater number of short chain branches in the polymer chains, the smaller the lamellar thickness [12,23]. Thus, the high temperature peaks of the sample correspond to unbranched or weakly branched molecules, the low temperature endotherms can be associated with more branched molecular species. As can be seen, despite the fact that the copolymers shown in Fig. 1 are obtained with homogeneous catalytic systems, none of them are homogeneous with regards to their compositions. All copolymers show multiple melting peaks on their DSC curves. However, the difference in the number of peaks, their location and their greatness of size can be observed. Catalysts B and C give copoly-

Table 2
DI values obtained for ethylene/1-hexene copolymers synthesised over various homogeneous metallocene catalysts

Catalyst composition	1-Hexene content (mol%)	DI values					
		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
Cp_2ZrCl_2/MAO	6.4	1.00	0.20	0.34	0.39	0.31	–
$(i\text{PrCp})_2ZrCl_2$/MAO	6.9	1.00	0.22	0.34	0.31	0.24	0.01
Ind_2ZrCl_2/MAO	6.7	1.00	0.17	0.22	0.25	0.02	0.02

mers with six peaks on their thermograms; between 98.6 and 127.8 °C for (B) and 94.5 and 128.6 °C for (C), although in the latter case a shoulder at the fourth peak can be observed. The first catalyst (A) produced copolymers with five separated peaks between 100.9 and 118.9. Unlike copolymers (B) and (C), the fraction containing unbranched or weakly branched macromolecules is not present in copolymer (A). The other copolymers contain one or two fractions of this type of macromolecule. For all copolymers considerable differences in size of the peaks can be also observed.

For the estimation of the heterogeneity of the ethylene/1-olefin copolymers the concept of the DSC index (DI) is very often used [4,15]. DI values can be obtained either through the calculation of the ratio of the peak height of each peak to the maximum peak in the thermogram of a polymer or, for more accurate weight distribution, the ΔH_{melt} for each fraction should be measured and used for DI calculation instead of peak height [15]. In our work, the later concept was applied. The comonomer distribution is considered to be homogeneous in cases where the DI values are all close to one [15]. The values of DI for copolymers obtained over the homogeneous catalysts A, B and C are presented in Table 2. In all cases the DI values are different for each peak, therefore the comonomer distribution along polymer backbone is heterogeneous. Among investigated copolymers, the most nearing DI values shows copolymer obtained with catalyst A, thus this copolymer can be consider as the most homogeneous one.

The next diagram (Fig. 2) presents the DSC curves of ethylene/1-hexene copolymers obtained over Cp_2ZrCl_2/MAO catalysts: homogeneous one (curve A) and those supported on inorganic carriers ($MgCl_2(THF)_2/Al(i\text{-}Bu)_3$ (curve B) and $MgCl_2(MeOH)_4/Al(i\text{-}Bu)_3$ (curve C)), after displaying the SSA procedure. It is clearly shown that the immobilization of the Cp_2ZrCl_2/MAO catalyst on magnesium chloride changed the properties of the synthesised copolymers. On the endotherms of both the copolymers synthesised with supported catalysts, there appears two additional peaks in comparison to their counterpart obtained over a homogeneous one. Like the previous catalytic system, the $(n\text{BuCp})_2ZrCl_2$/MAO (Fig. 3, curve A) catalyst after heterogenization on $MgCl_2(THF)_2/Al(i\text{-}Bu)_3$ (Fig. 3, curve B) also produced more heterogeneous copolymers. This same dependence is observed despite the fact that the copolymers produced with the last catalytic systems contained smaller amount of 1-hexene incorporated (about 4.5 instead of 6.5).

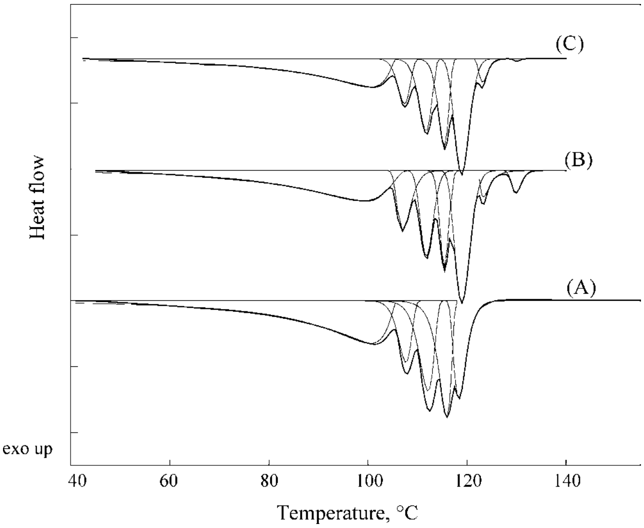


Fig. 2. Comparison of the melting curves of ethylene/1-hexene copolymers obtained with the homogeneous zirconocene catalyst Cp_2ZrCl_2/MAO (A) and its supported counterparts $MgCl_2(THF)_2/Al(i\text{-}Bu)_3/Cp_2ZrCl_2$/MAO (B), $MgCl_2(MeOH)_4/Al(i\text{-}Bu)_3/Cp_2ZrCl_2$ (C) using the SSA method for analysis.

The comparison of the melting curves of the copolymers obtained with homogeneous and heterogeneous catalysts shows that on the melting curve of copolymers synthesised with heterogeneous catalysts the additional peaks arise in the higher temperature region. The other big difference is that for the supported catalysts the fifth fraction has much higher contribution in comparison to the fifth fraction for the unsupported counterparts. And it also can be noted that the modification of magnesium chloride by tetrahydrofuran or methyl alcohol seems to not have a very important influence on the macromolecule's heterogeneity.

DI values obtained for ethylene/1-hexene copolymers synthesised with both the homogeneous catalyst and its supported counterparts (Table 3) indicate that none of the copolymers are homogeneous. DI values calculated for each fraction are different, although the greater dissimilarity is observed for the heterogeneous catalytic system.

As was explained before, comonomer incorporation into the polyethylene chain changes the ethylene sequence length. The many melting peaks observed in DSC heating curves arise due to the segregation of the crystallizable sequence

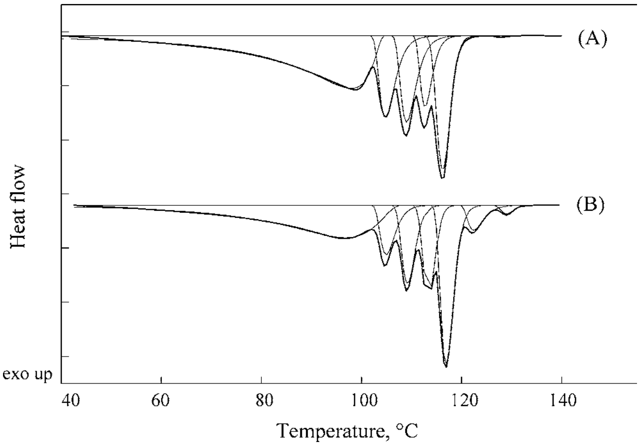


Fig. 3. Comparison of the melting curves of ethylene/1-hexene copolymers obtained with the homogeneous zirconocene catalyst $(n\text{BuCp})_2ZrCl_2$/MAO (A) and its supported counterpart $MgCl_2(THF)_2/Al(i\text{-}Bu)_3/(n\text{BuCp})_2ZrCl_2$/MAO (B) using the SSA method for analysis.

Table 3
Comparison of DI values obtained for ethylene/1-hexene copolymers synthesised over homogeneous and supported metallocene catalysts

Catalyst composition[a]	1-Hexene content (mol%)	DI values						
		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7
Cp_2ZrCl_2	6.4	1.00	0.20	0.34	0.39	0.31	–	–
$MgCl_2(THF)_2/Al(i\text{-}Bu)_3/Cp_2ZrCl_2$	6.7	1.00	0.25	0.33	0.26	0.61	0.09	0.07
$MgCl_2(MeOH)_4/Al(i\text{-}Bu)_3/Cp_2ZrCl_2$	6.3	1.00	0.19	0.32	0.32	0.59	0.07	0.01
$(n\text{BuCp})_2ZrCl_2$	4.9	1.00	0.25	0.26	0.17	0.35	–	–
$MgCl_2(THF)_2/Al(i\text{-}Bu)_3/(n\text{BuCp})_2ZrCl_2$	4.6	1.00	0.21	0.29	0.30	0.58	0.11	0.03

[a] Cocatalyst: MAO.

length. The longer segments recrystallized to longer lamellar crystals, which melt at a higher temperature. Thus, the number of peaks is related to the CCD [5].

The thickness of different lamellae can be calculated from the Thomson–Gibbs' equation [4]:

$$T_m = T_m^0 \left(\frac{1 - 2\delta_e}{\Delta H \times l_c} \right) \quad (1)$$

where T_m is the observed melting point (K), T_m^0 the equilibrium melting point of an infinite polyethylene crystal (414.5 K), δ_e the surface energy of a polyethylene crystal (70×10^{-3} J/m^2), ΔH the enthalpy of fusion of 100% crystalline polyethylene per unit volume (288×10^6 J/m^3), and l_c the thickness of the lamellae with melting point T_m (m)

The relative amount of lamellae of different thicknesses was calculated based on the area of the thermogram peaks. The lamellar thickness distributions in the copolymers obtained over the three homogeneous catalysts: Cp_2ZrCl_2/MAO (A), Ind_2ZrCl_2/MAO (B) and $(i\text{PrCp})_2ZrCl_2$/MAO (C) are presented in Fig. 4.

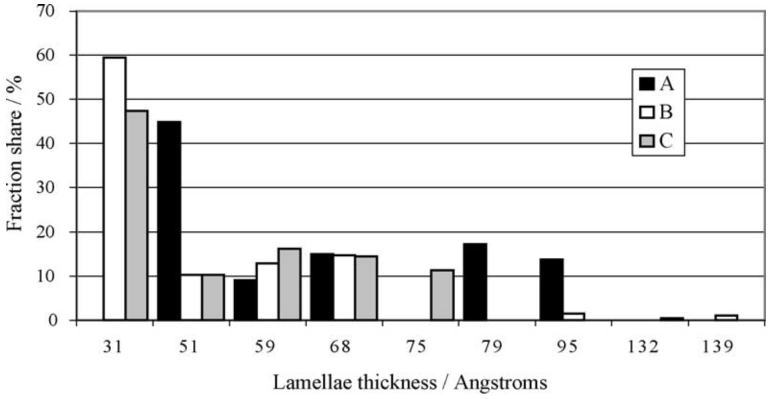


Fig. 4. Comparison of the share of lamellae with different thicknesses in ethylene/1-hexene copolymers obtained with homogeneous metallocene catalysts: $CpZrCl_2$/MAO (A), Ind_2ZrCl_2/MAO (B) and $(i\text{PrCp})_2ZrCl_2$/MAO (C).

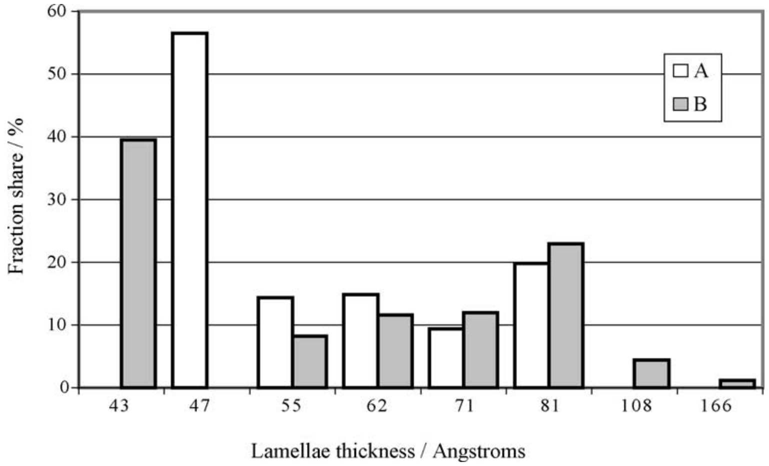


Fig. 5. Comparison of the share of lamellae with different thicknesses in ethylene/1-hexene copolymers obtained with the homogeneous catalyst $(n\text{BuCp})_2ZrCl_2$/MAO (A) and with the same catalyst supported on $MgCl_2(THF)_2/Al(i\text{-}Bu)_3$ (B).

As can be seen, the lamellae thickness greatly differs for these catalytic systems; the most varied lamellae thickness is shown by the copolymer synthesised with Ind_2ZrCl_2/MAO (from 31 to 139 Å) and the Cp_2ZrCl_2/MAO catalyst gives copolymers with the narrowest distribution of lamellae thickness (51–90 Å). In Fig. 5, the lamellae thickness in copolymers obtained with a $(n\text{BuCp})_2ZrCl_2$/MAO catalyst and its counterpart supported on $MgCl_2(THF)_2/Al(i\text{-Bu})_3$ are compared. As can be observed, the lamellae thickness varies from 47 to 81 Å and from 43 to 166 Å for copolymers obtained over homogeneous and supported catalyst, respectively. In both copolymers, the fractions with lamellae thicknesses about 45 Å clearly prevail. Their share, however, in each copolymer is different.

4. Conclusion

Our previous study revealed that a type of catalyst precursor, Ziegler–Natta or metallocene (VCl_4, Cp_2ZrCl_2), supported on $MgCl_2(THF)_2$ has a great influence not only on catalyst activity and its ability to incorporate comonomers but also on the compositional heterogeneity of copolymers [17,24]. The present results show that in the case of zirconocene catalysts, the type of ligand in L_2ZrCl_2 (Cp, Ind), as well as the presence of substituent R in the cyclopentadienyl ring evidently influence the compositional heterogeneity of ethylene/1-hexene copolymers. The amount of peaks on the DSC thermograms for copolymers, and their division, increase with the increase of bulkiness of ligand in the catalytic system. The copolymers with the narrowest CCD result from the Cp_2ZrCl_2/MAO catalyst. The heterogenization of metallocene compounds on inorganic carriers leads to an increase in the heterogeneity of the obtained copolymers, independent of the type of ligand in the zirconocene catalyst and the amount of 1-hexene incorporated. However, modification of the $MgCl_2$ carrier by tetrahydrofuran or methyl alcohol seems to not have any influence on the copolymers' CCD.

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