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The influence of cocatalysts on 1-hexene polymerization with various supported magnesium - titanium catalysts

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Summary

The influence of various cocatalysts on the activity and stereospecificity of a supported magnesium–titanium catalyst, generated by *in situ* reduction of titanium (IV) chloride using a Grignard reagent ($MgCl_2/TiCl_3$) or prepared by the recrystallization method ($MgCl_2$/2M2P/ED/$TiCl_4$, 2M2P = 2-methyl-2-pentanol, ED = dibutyl phthalate or ethyl benzoate), in the 1-hexene polymerization was investigated. The $MgCl_2/TiCl_3$ catalyst showed the highest activity but the lowest stereospecificity in the 1-hexene polymerization with all investigated cocatalysts. The $MgCl_2$/2M2P/ED/$TiCl_4$ catalyst with dibutyl phthalate as an internal electron donor was characterized by the highest stereospecificity and led to the polymers with high molecular weight. All catalysts showed the highest activity and stereospecificity when triisobutylaluminium was used as a cocatalyst. The addition of a small amount of ethyl benzoate as an external electron donor ([Al]/[ED] 10:1) led to considerable improvement of the stereospecificity of the $MgCl_2/TiCl_3$ catalyst in comparison with the catalysts prepared by the recrystallization method.

Introduction

At the present time investigations of the olefins polymerization and copolymerization using $MgCl_2$ – supported $TiCl_4$ catalyst systems attract significant attention [1–7]. Many studies are devoted to improvements of the activity and stereospecificity of catalysts [3-5, 8-10]. One of the key directions for such improvements is the proper selection of the combination of internal and external electron donors [5, 8, 9, 11-13]. The nature of cocatalyst also plays important role in the enhancement of the catalyst activity and stereospecificity [4, 10, 14]. However, the most of these studies involved the investigation of the propylene polymerization due to its commercial importance. On the contrary only a few articles concerning polymerization of the higher α-olefins catalyzed by the supported catalysts exist in the literature [14-17]. It should be noted that the investigations of the long-chain α-olefins (1-hexene, 1-octene) polymerization using a $MgCl_2$ – supported catalyst have an important role from standpoints of elucidating of their behavior by copolymerization with other olefins (ethylene, propylene). Moreover, high molecular weight homopolymers of the long-chain α-olefins are used as the lubricant oil additives.

As a rule the $MgCl_2$ – supported $TiCl_4$ catalyst systems exhibit very low catalytic activity in the polymerization of the higher α-olefins (10-30 g polymer/g Ti h) [15, 16] (with the exception of the $MgCl_2/TiCl_3/{}^iBu_3Al$ catalyst system (about 600 g polymer/g Ti h) [14]) in comparison to the propylene polymerization (up to 40-60 kg polymer/g Ti h) [5, 13, 18]. At the same time only several articles report about the tacticity of the polymers obtained from the higher α-olefins [15, 16, 19]. A vanadium-based catalyst system produces only 22–24 % of isotactic poly(1-octene) [19], the $TiCl_3{\cdot}3py/MgCl_2/AlEt_3$ catalyst system yields 45 % of isotactic poly(1-hexene) [16]. Recently, we have found out that the $TiCl_4/Al(C_6H_{13})_3{\cdot}Mg(C_6H_{13})_2$ catalyst system shows high activity in the 1-hexene polymerization (0.2 –1.2 kg polymer/g Ti h), but low stereospecificity (only 35 % of isotactic polymer is formed) [20]. On the other hand, the $MgCl_2$/2-ethyl-1-hexanol/EB/$TiCl_4/AlEt_3$ catalyst system prepared by the recrystallization method [8, 18, 21, 22] gives high isotactic poly(1-octene) (up to 74 %) [15]. In addition, it is known that in some cases usage of the bulky aluminium alkyls as a cocatalyst leads to enhancement of the activity and stereospecificity of the catalyst as well as of the molecular weight of the polymers [4, 10, 14].

In this work we study the influence of various cocatalysts on the activity and stereospecificity of the supported magnesium–titanium catalyst, generated by *in situ* reduction of titanium (IV) chloride using the Grignard reagent ($MgCl_2/TiCl_3$) or prepared by the recrystallization method ($MgCl_2$/2M2P/ED/$TiCl_4$, 2M2P = 2-methyl-2-pentanol, ED = dibutyl phthalate or ethyl benzoate), in the 1-hexene polymerization as well as on the molecular weight and molecular weight distribution of the obtained polymers.

Experimental

Materials

Anhydrous magnesium chloride was prepared according to [23] and was dried by heating at 150 ^{0}C under vacuum for 12 h. Ethyl benzoate was prepared by refluxing ethanol with benzoic acid. Ethyl benzoate, dibutyl phthalate and phenetole were purified by double distillation from CaH_2 under reduced pressure. 2-Methyl-2-pentanol was refluxed with BaO and distilled over CaH_2. Triethylaluminium and triisobutylaluminium were purified by distillation under reduced pressure and their purity was established by EDTA titration. Trihexylaluminium and magnesium aluminium alkyls ($AlMg(C_6H_{13})_5$) were synthesized following the procedure described in [24]. Tetraisobutylaluminoxane was prepared by the reaction of solid $MgCl_2{\cdot}6H_2O$ with triisobutylaluminium in *n*-hexane solution according to [10]. $TiCl_4$ was distilled from copper shavings under reduced pressure. *n*-Hexane and *n*-octane were treated with sulphuric acid until the acid layer remained colourless, then washed with aqueous $NaHCO_3$, dried over $CaCl_2$, and distilled from CaH_2 (at least twice) under inert atmosphere. 1-Hexene (Aldrich) was distilled over CaH_2 under argon atmosphere. *n*-Butyl chloride was dried with $CaCl_2$ and distilled over CaH_2. Standard Schlenk techniques and high-purity argon were used for handling all compounds.

Instruments

The contents of Ti and Mg in the catalysts were determined by atomic emission spectrophotometry with an ICP/AES SpecrtoFlame, Spectro GmbH instrument.

Chloride was determined by back titration according to the Volhard's method. The intrinsic viscosity of the obtained polymers was measured in cyclohexane at 25±0.1 ^{0}C using an Ubbelohde viscosimeter. The molecular weights (M_η) of the polymers were calculated using the formula which has been reported before [25]. Size exclusion chromatography (SEC), was performed on a Spectra Physics apparatus with two columns (PL gel, 5 µm, 300 mm, 500 Å and 100 Å) and one pre-column (PL gel 5 µm guard). The detection was achieved with a SP8430 differential refractometer. THF was eluted at the flow rate of 0.8 mL/min. The calculation of molecular weight (M_w) and polydispersity (M_w/M_n) was based on polystyrene standards. The ^{13}C NMR spectra of polymers were recorded on a Bruker AC-400 spectrometer in $CDCl_3$ solution operating at 100.6 MHz at 25 ^{0}C. The amount of isotactic polymer was determined by the cutting–weighing method. DSC analyses were performed on a Mettler Toledo instrument using the 10 ^{0}C min^{-1} heating rate. The quantities of the organic components in the catalysts were determined by hydrolysis-gas chromatography (GC) using quartz capillary column DB-5 (l=30 m; 0.54 mm ID; 1.5 µm df) with a Shimadzu GC-17AAF/APC chromatograph programmed from 40 ^{0}C to 280 ^{0}C at 8 ^{0}C/min. The injection port temperature and the detector temperature was 280 ^{0}C. About 0.1 g of the catalyst was dissolved in 5 mL of 1N HCl and extracted thrice by 5 mL of ether. Control experiments with known quantities of ethyl benzoate, dibutyl phthalate and 2-methyl-2-pentanol showed that they quantitatively extracted from 1N HCl by ether.

Preparation of catalysts and polymerization procedure

The $MgCl_2/TiCl_3$ catalyst (Cat–A) was prepared by *in situ* reduction of titanium (IV) chloride using the Grignard reagent following the procedure described earlier [14]. Cat–B and Cat–C were prepared as follows: 0.7 g (7.4 mmol) of anhydrous $MgCl_2$ and 9.2 mL (74 mmol) of 2-methyl-2-pentanol were added to the reactor which was previously dried and purged with argon. The reactor was kept at 100 ^{0}C for 2 h, then 0.74 mmol of the electron donor (dibutyl phthalate or ethyl benzoate) was added, stirred at 115 ^{0}C for an additional 1 h and 50 mL of *n*-octane was introduced to the reaction mixture. Then the solvent was evaporated until getting a white solid product. The recrystallized support was washed two times with *n*-hexane in order to extract the remained alcohol. Then this support was activated with 4.5 mL (0.041 mol) $TiCl_4$ at 70 ^{0}C for 2 h, washed six times with *n*-hexane in order to remove the excess of $TiCl_4$. Finally, the catalysts were dried in vacuum.

Required amounts of the catalyst, solvent and monomer were added to the reactor which was previously vacuumed and purged with argon. Time, when the desired amount of the cocatalyst was added to the reaction mixture, was defined as starting time of the polymerization. The polymerization was stopped by adding of acidified ethanol. The obtained polymer was washed with ethanol and dried to constant weight. Specific reaction conditions are listed in tables or figure captions.

Results and discussion

Table 1 shows the results of the elemental analysis of four supported catalysts which have been used in this work.

Cat–A was prepared by *in situ* reduction of $TiCl_4$ by means of the Grignard reagent, while Cat–D was synthesized using original (not recrystallized) $MgCl_2$. Cat–B and

Table 1. Composition and abbreviation of the prepared catalysts [a)]

Catalyst	Catalyst code	Ti (wt %)	Mg (wt %)	Cl $_{exp}$ (wt %)	Cl $_{calc}$ (wt %)
$MgCl_2/TiCl_3$	Cat-A	6.4	19.4	61.9	58.0
$MgCl_2$/2M2P/DBP/$TiCl_4$	Cat-B	6.1	17.5	56.6	59.4
$MgCl_2$/2M2P/EB/$TiCl_4$	Cat-C	12.0	16.5	64.1	81.0
$MgCl_2$/DBP/$TiCl_4$	Cat-D	6.7	15.8	60.1	58.4

[a)] 2M2P – 2-methyl-2-pentanol, DBP – dibutyl phthalate; EB – ethyl benzoate

Cat–C were obtained by the recrystallization method. As it has been already reported the alcohols with higher carbon numbers and branching, when they are used for dissolving anhydrous $MgCl_2$ in the recrystallization method, are more efficient in the obtaining the highly active supported catalysts [15, 21]. Therefore, in our study for recrystallization of $MgCl_2$ we used 2-methyl-2-pentanol.

As it can be seen from table 1, all catalysts are characterized by the high Ti contents. It is interesting to note that the catalyst obtained by recrystallization from 2-methyl-2-pentanol with ethyl benzoate as an internal electron donor (Cat–C) contains twice as much Ti than the catalyst prepared with dibutyl phthalate (Cat–B). A comparison between the chlorine contents, found experimentally and those calculated ([Cl]=2[Mg]+3[Ti] for Cat-A and [Cl]=2[Mg]+4[Ti] for Cat–B, Cat–C and Cat–D), showed good agreement for Cat–A, Cat-B and Cat–D, but lower value for Cat–C. It can be associated with the formation of titanium alkoxides in the course of $TiCl_4$ impregnation into $MgCl_2$. The liberation of HCl during the catalyst preparation clearly indicated on the reaction of $TiCl_4$ with alcohol which remains after solvent evaporation from recrystallized $MgCl_2$ [18, 21]. The liberation of HCl was not detected when not recrystallized $MgCl_2$ was used as the support. These data point out that only a part of fixed titanium tetrachloride on $MgCl_2$ is actually active in the polymerization, because titanium alkoxides don’t participate in the formation of active sites [21].

The GC analysis shows that the most of complexed alcohol was removed from the support after washings with *n*-hexane and vacuum drying (table 2). The small amount of ethyl benzoate in comparison with dibutyl phthalate was detected in the catalysts, indicating that EB was complexed with support in a much smaller extent than DBP. As observed in table 2, 2-methyl-2-pentanol was removed almost completely from the support and only half of the introduced electron donor remains after treatment with $TiCl_4$. Therefore, the concentration of titanium alkoxides, formed during the interaction of $TiCl_4$ with support, can be estimated using the concentration of alcohol which remains in the support.

Table 2. The organic components in the support and supported catalysts by GC

Support or catalyst	2-Methyl-2-pentanol (μmol/g)	Electron donor (mmol/g)
$MgCl_2$/2M2P/EB	23	0.087
Cat-B	0.9	0.725
Cat-C	0.8	0.046

All prepared catalysts were tested in the 1-hexene polymerization. Table 3 shows the results obtained in the polymerization of 1-hexene with various cocatalysts.

Table 3. The effect of the nature of the catalyst and cocatalyst on the catalytic activity, molecular weight and isotacticity of the polymers [a)]

Catalyst system	Activity (g poly(1-hexene)/g Ti h)	Conversion (%)	M_η x10^{-4} b)	M_w x10^{-4} c)	M_w/M_n	mmmm d) (%)
Cat-A/Et_3Al	97.9	85.3	4.2	5.9	6.60	43
Cat-A/$^iBu_3Al$	97.8	84.0	7.3	11.4	4.4	55
Cat-A/$^iBu_3Al$ e)	391	33.5	24.0	33.8	3.45	50
Cat-A/ $(^iBu_2Al)_2O$	97.6	84.0	30.2	34.4	3.02	43
Cat-A/ $AlMg(C_6H_{13})_5$ f)	56.9	49.2	97.7	32.7	4.0	52
Cat-B/Et_3Al	10.5	24.9	19.1	20.6	5.15	55
Cat-B/$^iBu_3Al$	19.5	45.7	132.4	40.0	3.32	67
Cat-B/ $(^iBu_2Al)_2O$	11.7	28.1	208.9	77.3	3.10	50
Cat-B/ $Al(C_6H_{13})_3$ g)	0.5	7.3	134.9	–	–	–
Cat-B/ $AlMg(C_6H_{13})_5$	0.7	1.7	75.5	–	–	–
Cat-C/Et_3Al	6.4	29.7	10.4	10.8	2.79	56
Cat-C/$^iBu_3Al$	16.3	72.9	29.4	–	–	65
Cat-C/ $AlMg(C_6H_{13})_5$	0.6	4.0	99.1	23.5	2.3	–
Cat-D/ $^iBu_3Al$	13.3	15.1	–	107.4	2.17	–

[a)] [1-Hexene] 1 mol·L^{-1}; [Ti] 7.7 10^{-3} (Cat–A), 20 10^{-3} (Cat–B), 40 10^{-3} (Cat–C); [Al]/[Ti] 35 (Cat–A), 15 (Cat–B, Cat–D), 5 (Cat–C); T 40 ^{0}C, time 2 h. [b)] Determined by viscosimetry. [c)]Determined by SEC [d)] Determined by ^{13}C NMR. [e)] [Ti] 0.9 10^{-3} mol·L^{-1}. [f)] [1-Hexene] 2 mol·L^{-1}. [g)] Time 9 h

As it has been already reported in the Introduction, the $MgCl_2/TiCl_3/^iBu_3Al$ catalyst system shows the highest activity toward 1-hexene polymerization (about 600 g polymer/g Ti h) [14] among $MgCl_2$ – supported $TiCl_4$ catalysts. However, there is no information about the microstructure of the obtained polymers. Taking into account that the use of bulky aluminium alkyls in some cases can lead to the increase in the stereospecificity of the catalyst [10], we study the influence of various cocatalysts on the stereospecificity and activity of the $MgCl_2/TiCl_3$ (Cat–A) catalyst as well as on the molecular weight and polydispersity of the obtained polymers. We have found out that Cat–A produces polymers with low degree of the isotacticity. From the ^{13}C NMR analysis, the [*mmmm*] pentad fractions were estimated to be about 40 – 55 % for the various cocatalysts. Among investigated cocatalysts $^iBu_3Al$ gave more isotactic polymer (table 3). The utilization of bulky tetraisobutylaluminoxane ($(^iBu_2Al)_2O$) or magnesium aluminium alkyls ($Al(C_6H_{13})_3 \cdot Mg(C_6H_{13})_2$) as the cocatalysts doesn't lead to improvement of the stereospecificity of Cat–A (see table 3). On the other hand, the highest molecular weight product was obtained when these cocatalysts were used for activation of Cat-A that can indicate on the higher ability of $^iBu_3Al$ and especially of Et_3Al in the chain transfer reactions in comparison with $(^iBu_2Al)_2O$ and $Al(C_6H_{13})_3 \cdot Mg(C_6H_{13})_2$. In general, the obtained results show that the increase in bulkiness of the cocatalyst leads to the increase in the molecular weight and narrowing of the molecular weight distribution of the obtained polymers that is in agreement with the data of other authors [4, 14, 17]. It also should be noted that the molecular weight of the polymers (M_w) determined by SEC is in good agreement with that obtained by viscosimetry for the low molecular weight poly(1-hexene)s (M_η up to $30 \cdot 10^4$) and considerably lower for the high molecular weight poly(1-hexene)s ($M_\eta > 30 \cdot 10^4$). This difference in molecular weight determined by viscosimetry and SEC is likely because M_w was calculated on the basis of polystyrene calibration. In addition, the $MgCl_2/TiCl_3$ catalyst showed almost the same activity (about 100 g poly(1-hexene)/g Ti h) with all cocatalysts with the exception of $Al(C_6H_{13})_3 \cdot Mg(C_6H_{13})_2$ and the activity of the $MgCl_2/TiCl_3/{}^iBu_3Al$ catalyst system obtained in this work is comparable with the activity obtained earlier for this catalyst system [14] if the similar [Ti]/[M] ratio was used (table 3).

Table 4. The influence of the external electron donor on the catalytic activity, molecular weight and isotacticity of the polymers [a)]

Catalyst system	Activity (g poly(1-hexene)/g Ti h)	Conversion (%)	M_η x10^{-4} [b)]	M_w x10^{-4} [c)]	M_w/M_n	mmmm [d)] (%)
Cat-A/$^iBu_3Al$	97.8	84.0	7.3	5.9	6.60	55
Cat-A/ $^iBu_3Al$/EB	44.8	76.5	25.1	21.3	5.60	82
Cat-B/$^iBu_3Al$	19.5	45.7	132.4	40.0	3.32	67
Cat-B/ $^iBu_3Al$/EB	11.0	25.8	150.3	41.8	3.27	68
Cat-C/$^iBu_3Al$	16.3	72.9	29.4	22.9	3.18	65
Cat-C/ $^iBu_3Al$/EB	8.6	39.6	108.9	30.1	2.59	67
Cat-C/ $^iBu_3Al$/PhOEt	16.8	74.9	30.4	–	–	67

[a)] [1-Hexene] 1 mol·L^{-1}; [Ti] 7.7 10^{-3} (Cat–A), 20 10^{-3} (Cat–B), 40 10^{-3} (Cat–C); [Al]/[Ti] 35 (Cat–A), 15 (Cat–B), 5 (Cat–C); [Al]/[ED] 10:1; T 40 ^{0}C, time 2 h. [b)] Determined by viscosimetry. Determined by SEC. [d)] Determined by ^{13}C NMR. EB – ethyl benzoate. PhOEt – phenetole

It is worth noting that the addition of the external electron donor (EB) to the $MgCl_2/TiCl_3/{}^iBu_3Al$ catalyst system leads to the considerable increase in the stereospecificity of the catalyst (see table 4). Such modification of Cat–A also allows to increase significantly the molecular weight and narrow the molecular weight distribution of the polymers but the activity of the catalyst decreases approximately by a factor of two.

In the course of our further investigations we will examine the 1-hexene polymerization with a catalyst prepared by the recrystallization method. Recently, we have found out that the catalysts obtained by recrystallization of $MgCl_2$ from ethanol as well as from 2-methyl-2-pentanol without internal electron donor show the low activity and stereospecificity in the 1-hexene polymerization [26]. We have also reported that the $MgCl_2$/2M2P/ED/$TiCl_4/{}^iBu_3Al$ (ED = DBP or EB) catalyst system exhibits the maximum activity at the low Al/Ti ratios (Al/Ti = 5–15) [26]. As it has been mentioned above the part of the fixed titanium tetrachloride on $MgCl_2$ is inactive in the 1-hexene polymerization due to the formation of titanium alkoxides during the catalyst preparation. Therefore, the real Al/Ti ratios exceed the mentioned above values.

As it can be seen from table 3 the catalysts prepared by the recrystallization method (Cat–B and Cat–C) as a rule were significantly less active (up to 20 g poly(1-hexene)/g Ti h) than the catalyst obtained by the reduction of titanium tetrachloride with the Grignard reagent. Moreover, the catalyst Cat–D, prepared using not recrystallized $MgCl_2$, shows lower catalytic activity than Cat–B and Cat–C. On the other hand, Cat–B leads to the polymers with higher molecular weight in comparison with Cat–A. The highest molecular weight polymer was obtained with the Cat–B/$(^iBu_2Al)_2O$ catalyst system. In addition, as in the case of the polymerization of 1-hexene with Cat-A, the usage of a bulky cocatalyst leads to the increase in the molecular weight and narrowing of the molecular weight distribution of the polymers obtained (table 3).

The data of table 3 also indicate that Cat–B and Cat–C were characterized by the higher stereospecificity with $^iBu_3Al$ as the cocatalyst than that with $AlEt_3$. Among supported catalysts, prepared by the recrystallization method, the ability to produce isotactic polymer increased for the following range: $MgCl_2/2M2P/TiCl_4$ (43 % for $AlEt_3$ and 50 % for $^iBu_3Al$) [26] < $MgCl_2/2M2P/DBP/TiCl_4$ (55 % for $AlEt_3$ and 67 % for $^iBu_3Al$) ~ $MgCl_2/2M2P/EB/TiCl_4$ (56 % for $AlEt_3$ and 65 % for $^iBu_3Al$). These results show good agreement with the results of the 1-octene polymerization using the $MgCl_2$/2-ethyl-1-hexanol/DBP/$TiCl_4/AlEt_3$ catalyst system [15] with the exception of the polymerization with the $MgCl_2$/2-ethyl-1-hexanol/EB/$TiCl_4/AlEt_3$ catalyst system (74 % of isotactic poly(1-octene) was obtained). The use of the other cocatalysts ($Al(C_6H_{13})_3$, $(^iBu_2Al)_2O$ and $AlMg(C_6H_{13})_5$) doesn't improve the catalyst activity and its stereospecificity (table 3). Moreover, as it can be seen from table 4, the addition of EB as the external electron donor almost doesn't have any positive effect on the stereospecificity of Cat–B and Cat–C in comparison with Cat–A but leads to the decrease in the catalyst activity. On the other hand, the use of EB results in the considerable increase in the molecular weight and narrowing of the molecular weight distribution for Cat-C in comparison with Cat-B, most likely due to the low concentration of the internal electron donor in Cat-C (see table 2). Interestingly, the utilization of phenetole affects neither the stereospecificity nor the catalyst activity and molecular weight.

The obtained results confirm the hypothesis that the main function of the internal and external electron donor is the same or similar [5]. Indeed, the catalysts prepared by different methods without internal electron donor possess similar stereospecificity: 55 % and 50 % of isotactic polymer are formed with $MgCl_2/TiCl_3/^iBu_3Al$ and $MgCl_2/2M2P/TiCl_4/^iBu_3Al$ catalyst systems, respectively. The use of EB as the internal ($MgCl_2/2M2P/TiCl_4$ catalyst) or external ($MgCl_2/TiCl_3$ catalyst) electron donor leads to almost comparable increase in isotacticity of the obtained poly(1-hexene)s (see table 4). Moreover, the addition of EB as an external donor to the $MgCl_2/2M2P/EB/TiCl_4$ catalyst (EB is relatively efficient isotacticity improver for the catalyst with EB as the internal electron donor [12]) doesn't change in the isotacticity. Evidently, when EB are added as the external electron donor (Cat-A), it has some poisoning effect that results in the considerable decrease in activity of the catalysts. The addition of the electron donor leads not only to the noticeable increase in isotactic fraction, but to the considerable increase in the molecular weight and narrowing of the molecular weight distribution of poly(1-hexene)s obtained (see figure 1). It points out that internal or external electron donor directly takes part in the formation of isospecific active centers [11]. Moreover, these centers are more stable than ones without electron donor that allows to obtain the polymers with higher molecular weight. Another explanation is that the electron donor decreases the concentration of the active centers due to the interaction with them that leads to the increase of molecular weight. In addition, taking into account that steric bulkiness of the aluminium alkyls influences the stereospecificity of the catalysts we can conclude that a cocatalyst can participate in the formation of isospecific active center.

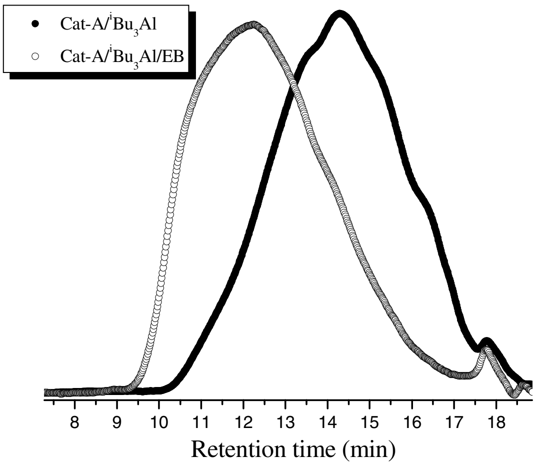

Figure 1. SEC traces of poly(1-hexene)s obtained by the $MgCl_2/TiCl_3/^iBu_3Al/$ catalyst system with and without ethyl benzoate as the external electron donor.

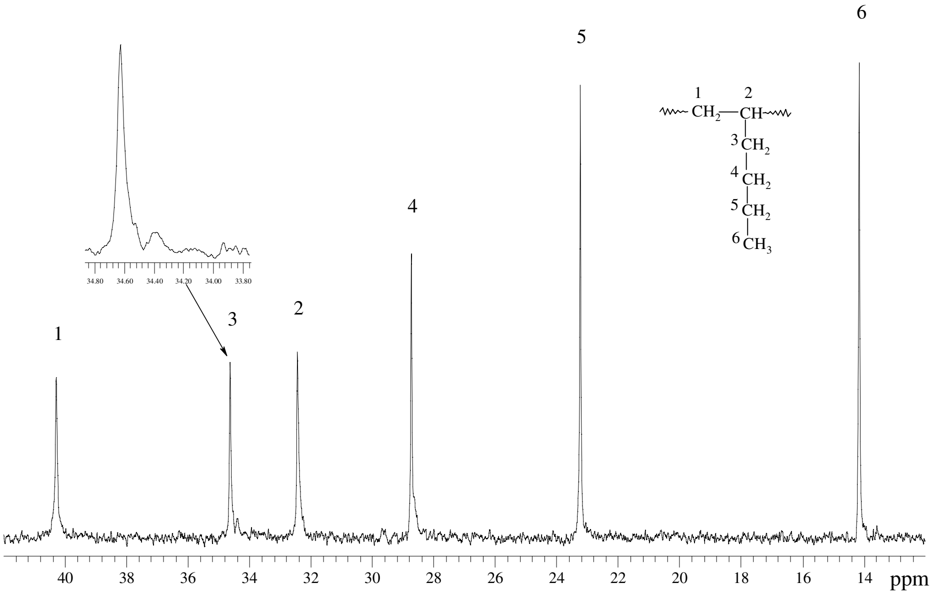

Figure 2. ^{13}C NMR spectrum of poly(1-hexene) prepared by the $MgCl_2/TiCl_3/^iBu_3Al/EB$ catalyst system.

Figure 2 shows typical ^{13}C NMR spectrum of poly(1-hexene) prepared with the $MgCl_2/TiCl_3/^iBu_3Al/EB$ catalyst system. There are six signals arising from six different carbon atoms in the spectrum. The multiplicity of the C^3 carbon atom has been used for quantitative examination of the stereoregularity of the obtained poly(1-hexene). The signal which arises due to isotactic pentad sequence [*mmmm*] is identified according to the earlier report [15, 27]. It should be mentioned that no resonance lines corresponded to endgroups and branches are found for this sample.

The thermal properties of poly(1-hexene) with the degree of isotacticity about 50 % obtained with the $MgCl_2/TiCl_3/^iBu_3Al$ catalyst system was examined by means of DSC analysis. DSC record is shown in Figure 3. The analyzed poly(1-hexene) shows only glass-transition temperature at –50.86 ^0C that is in good agreement with the earlier obtained data [28, 29].

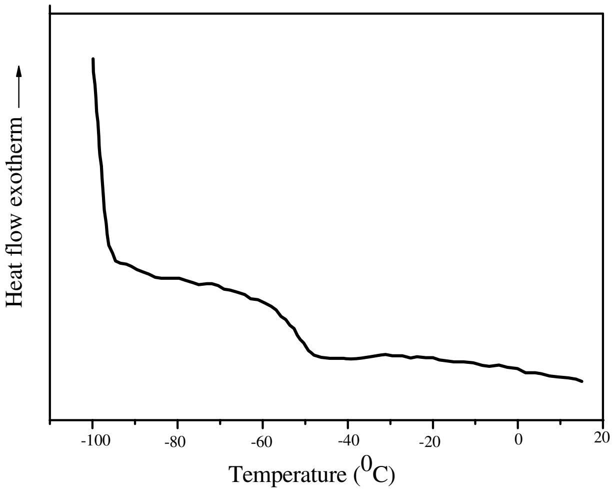

Figure 3. DSC trace of poly(1-hexene) obtained with the $MgCl_2/TiCl_3/^iBu_3Al$ catalyst system.

Conclusions

In the 1-hexene polymerization the $MgCl_2/TiCl_3$ catalyst showed the higher activity in comparison with the catalysts prepared by the recrystallization method. Among various cocatalysts used, triisobutylaluminium in conjunction with supported magnesium–titanium catalysts showed the highest activity and stereospecificity while $(^iBu_2Al)_2O$ and $Al(C_6H_{13})_3{\cdot}Mg(C_6H_{13})_2$ produced poly(1-hexene) of the highest molecular weight. The $MgCl_2/2M2P/ED/TiCl_4$ catalyst with dibutyl phthalate as the internal electron donor allows producing of the highest molecular weight polymers. Among the investigated catalysts ability to yield isotactic polymer increased in the following order: $MgCl_2/TiCl_3/^iBu_3Al$ < $MgCl_2/2M2P/EB/TiCl_4/^iBu_3Al$ ~ $MgCl_2/2M2P/DBP/TiCl_4/^iBu_3Al$ < $MgCl_2/TiCl_3/^iBu_3Al/EB$. The addition of ethyl benzoate as the external electron donor ([Al]/[ED] 10:1) has a pronounced effect on the stereospecificity of the $MgCl_2/TiCl_3$ catalyst but doesn't have any positive effect in the case of the catalysts prepared by the recrystallization method.

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