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Chloroaluminate ionic liquids as a medium of titanocene catalyst activated by alkyl aluminum compounds for ethylene polymerization

Summary — 1-Ethyl-3-methylimidazolium tetrachloroaluminate ($[\text{EMIM}]^+[\text{AlCl}_4]^-$) and 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate ($[\text{BMIM}]^+[\text{AlCl}_4]^-$) ionic liquids were applied in biphasic ethylene polymerization as a medium of Cp_2TiCl_2 titanocene catalyst. The effects of alkylaluminum compound (MAO, AlEt_3 , AlEt_2Cl , AlEtCl_2), the activator/catalyst molar ratio, polymerization time, ethylene pressure, catalyst recycling and the volume of the ionic liquid/hexane medium on the polymerization yield were investigated. Physical properties of polyethylene (PE) obtained are presented. It was shown that AlEtCl_2 is the best activator investigated so far. The $[\text{BMIM}]^+[\text{AlCl}_4]^-$ ionic liquid is a better medium for the titanocene catalyst than $[\text{EMIM}]^+[\text{AlCl}_4]^-$ one. The product obtained is characterized primarily by its high crystallinity degree and shows the properties of a typical linear polyethylene. Thus, biphasic ionic liquid polymerization of ethylene can be a potential alternative to that with a metallocene catalyst immobilized on a solid carrier.

Key words: ethylene polymerization, ionic liquids, metallocene catalyst, biphasic process, polyethylene properties.

CHLOROGLINIANOWE CIECZE JONOWE JAKO ŚRODOWISKO POLIMERYZACJI ETYLENU PROWADZONEJ WOBEC KATALIZATORA TYTANOCENOWEGO AKTYWOWANEGO ZWIĄZKAMI GLINOORGANICZNYMI

Streszczenie — Ciecze jonowe — mianowicie tetrachlorogliniany: 1-etylo-3-metyloimidazoliowy ($[\text{EMIM}]^+[\text{AlCl}_4]^-$) oraz 1-*n*-butylo-3-metyloimidazoliowy ($[\text{BMIM}]^+[\text{AlCl}_4]^-$) — użyto w procesie dwufazowej polimeryzacji etylenu w charakterze medium katalizatora tytanocenowego Cp_2TiCl_2 aktywowanego różnymi związkami glinoorganicznymi (rys. 1). Zbadano wpływ zastosowanego aktywatora [(MAO (metyloalumoksanu), AlEt_3 , AlEt_2Cl lub AlEtCl_2)], stosunku molowego Al/Ti, czasu reakcji, ciśnienia etylenu, ponownego użycia katalizatora (recyklingu) oraz objętości zarówno cieczy jonowej, jak i fazy heksanowej na wydajność reakcji polimeryzacji (tabele 1–3). Przedstawiono wybrane właściwości fizyczne otrzymanych próbek polietylenu (tabela 4). Wykazano, że najefektywniejszym spośród użytych aktywatorów jest AlEtCl_2 a $[\text{BMIM}]^+[\text{AlCl}_4]^-$ stanowi lepsze środowisko omawianej dwufazowej polimeryzacji niż $[\text{EMIM}]^+[\text{AlCl}_4]^-$. Uzyskiwany polimer charakteryzuje się dużym stopniem krystaliczności i właściwościami typowymi dla liniowego polietylenu. Polimeryzacja dwufazowa staje się zatem alternatywą dla dotychczasowej polimeryzacji prowadzonej przy użyciu katalizatorów metalocenowych na stałym nośniku.

Słowa kluczowe: polimeryzacja etylenu, ciecze jonowe, katalizator metalocenowy, proces dwufazowy, właściwości polietylenu.

Ionic liquids, *i.e.* salts that are liquid at temperature close to room temperature, are presently attracting a great interest [1–4]. Having a polar but weakly coordinating character as well as being non-volatile and immiscible with numerous organic solvents, ionic liquids are promising as solvents for many catalytic reactions [5]. Particularly, they seem to be excellent for non-aqueous polar biphasic processes, mainly because the pro-

ducts can easily be separated by simple decantation and both the catalyst and the ionic liquid can be reused in multicycle reactions.

In our previous report, 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate ($[\text{BMIM}]^+[\text{AlCl}_4]^-$) was applied to biphasic ionic liquid/hexane ethylene polymerization as a medium of Cp_2TiCl_2 titanocene catalyst activated by MAO, AlEt_3 or AlEt_2Cl alkylaluminum compounds [6]. The results showed that biphasic ionic liquid polymerization of ethylene with a use of metallocene catalyst is possible and offers interesting technological implications.

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An advantageous feature of the ionic liquids is the possibility to change or modify both the cations and anions, and in consequence, to tailor the reaction environment so as to enhance catalyst performance. This work is a continuation of our studies and describes how the Cp_2TiCl_2 catalyst activated by alkylaluminum compound behaves in biphasic process of ethylene polymerization in the presence of tetrachloroaluminate ionic liquid having a methylimidazolium cation substituted by either ethyl or *n*-butyl chain ($[\text{EMIM}]^+[\text{AlCl}_4]^-$ or $[\text{BMIM}]^+[\text{AlCl}_4]^-$ respectively). Additionally, AlEtCl_2 was investigated as an activator. The properties of polyethylene obtained are also presented.

EXPERIMENTAL

Materials

— Ethylene (Petrochemia SA, Płock) and pure nitrogen (Polgaz) were used after having been passed through a column of sodium metal supported on Al_2O_3 .

— Pure-grade hexane (POCH, Gliwice) was refined with sulfuric acid, dried by refluxing in argon from the sodium metal, and stored over 4A molecular sieves.

— Bis(cyclopentadienyl)titanium(IV) dichloride (Cp_2TiCl_2 , Aldrich), methylalumoxane (MAO, as 10 wt. % toluene solution, Aldrich), triethylaluminum (AlEt_3), diethylaluminum chloride (AlEt_2Cl) and ethylaluminum dichloride (AlEtCl_2) (all three 1M as hexane solutions, Aldrich), 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate ($[\text{BMIM}]^+[\text{AlCl}_4]^-$, Aldrich, assay ≥ 95 wt. %), 1-ethyl-3-methylimidazolium tetrachloroaluminate ($[\text{EMIM}]^+[\text{AlCl}_4]^-$, Aldrich, ≥ 95 wt. %), HCl 35–38 wt. %, H_2SO_4 98 wt. %, and HF 40 wt. % (all three POCH, Gliwice) were applied as purchased.

— 1,2,4-Trichlorobenzene (TCB, 99 wt. %, Aldrich) was purified by distillation.

Ethylene polymerization

All steps were carried out in oxygen-free conditions using an inert nitrogen atmosphere. The alkylaluminum compound (MAO , AlEt_3 , AlEt_2Cl , AlEtCl_2) was added to both the ionic liquid and hexane phases to act not only as an activator but also as a scavenger of impurities. The alkylaluminum compound was added to the ionic liquid in molar ratio 1/10. The mixture was left until water was completely removed what had been determined by FTIR.

A typical polymerization reaction was conducted in a 500 ml glass reactor (Büchi) equipped with a mechanical stirrer and a water jacket to maintain constant temperature. The previously prepared mixture of the ionic liquid (5 ml)/alkylaluminum compound ($2 \cdot 10^{-3}$ mol of Al) containing Cp_2TiCl_2 ($1.2 \cdot 10^{-4}$ mol) and hexane (150 ml) containing the alkylaluminum compound ($2 \cdot 10^{-4}$ mol of Al) were added successively into the reactor under a

nitrogen atmosphere and the ethylene was bubbled through the reaction mixture at pressure 0.1 or 0.5MPa while the temperature 30 °C was maintained. The polymerization reaction was terminated by ethylene feed stopping, decantation of the hexane phase and, finally, by adding 5 % solution of hydrochloric acid in methanol to both the hexane and ionic liquid phases. The polymer was filtered off, washed with methanol and dried.

Catalyst recycling

When the experiment of the catalyst recycling was performed, the cycle of the polymerization reaction was terminated by stopping of ethylene feed and decantation of the hexane phase while the ionic liquid phase containing the catalyst remained in the reactor. Then, a new hexane portion (150 ml) containing the alkylaluminum compound ($2 \cdot 10^{-4}$ mol of Al) was added and the reaction was carried out again as mentioned above.

Methods of polymer characterization

— The FTIR analysis carried out using a “Philips Analytical PU 9800” spectrometer (resolution $R = 2 \text{ cm}^{-1}$, bands 4000—400 cm^{-1}) in Nujol KBr/KBr.

— The molecular weight and molecular weight distribution of each polymer sample were determined by gel permeation chromatography (GPC, “Waters 150-CV”) using 1,2,4-trichlorobenzene as a solvent at 142 °C. The data were analyzed using polystyrene calibration curves.

— The degree of crystallinity (*C*) and melting temperature of polyethylene were estimated using a DSC 2010 TA instrument. *C* value was calculated using the equation:

$$C = (\Delta h_f / \Delta h_{f,c}) \cdot 100 \% \quad (1)$$

where: Δh_f — heat of fusion of polyethylene sample, $\Delta h_{f,c}$ — heat of fusion of standard.

The linearity of polyethylene was analyzed using a “Nicole Nexus 2002 FTIR” spectrometer. The samples, in the form of tablets, consisted of polyethylene powder and KBr. The number of branches in polyethylene was estimated on the basis of the ratio of the band at 1379.3 cm^{-1} and band at 1368.7 cm^{-1} . The former band results mainly from the presence of methyl groups in the branches. The latter is the band of absorption of methylene groups.

— Bulk density of polyethylene was determined according to the Polish Standard PN-80/C-04532.

RESULTS AND DISCUSSION

Ionic liquid

$[\text{EMIM}]^+[\text{AlCl}_4]^-$ is a liquid of brownish color, well dissolved in acetone, toluene or chloroform, but not dis-

solved in hexane or diethyl ether. Both $[\text{EMIM}]^+[\text{AlCl}_4]^-$ and $[\text{BMIM}]^+[\text{AlCl}_4]^-$ react rapidly with water, methanol, and to some extent when exposed to an air. Commercial chloroaluminate ionic liquids contain traces of water, what is toxic for the catalyst studied. This can be eliminated by adding of an alkylaluminum compound, which can be confirmed by FTIR (lack of band at $3000\text{--}3500\text{ cm}^{-1}$). The alkylaluminum compound, as a Lewis acid, increases the acidity of commercial, neutral chloroaluminate ionic liquids [7]. It should be noted, however, that it is advantageous for olefin oligomerization and polymerization taking place in the acidic ionic liquids [8, 9].

Biphasic process

Figure 1 shows the biphasic system of ethylene polymerization described herein. The ionic liquids, $[\text{EMIM}]^+[\text{AlCl}_4]^-$ or $[\text{BMIM}]^+[\text{AlCl}_4]^-$, were applied as a phase of Cp_2TiCl_2 titanocene catalyst and alkylaluminum activator such as MAO, AlEt_3 , AlEt_2Cl or AlEtCl_2 . Another phase was hexane with a small amount of alkylaluminum compound introduced to act as a

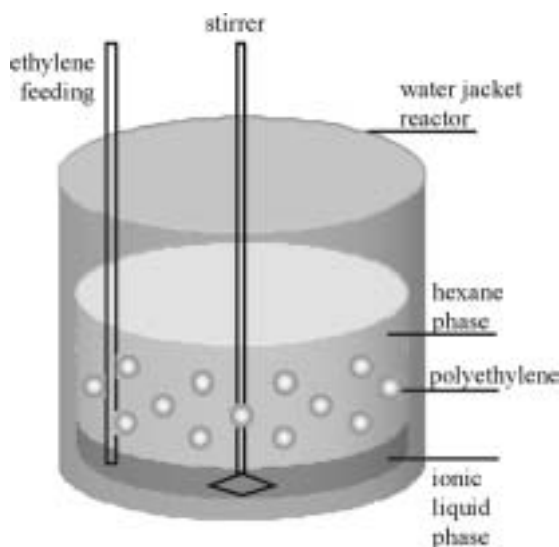


Fig. 1. Scheme of biphasic ionic liquid/hexane system in ethylene polymerization.

scavenger of impurities. The ionic liquid phase, having the alkylaluminum compound, is brown at the beginning of the reaction but becomes brown-green when Cp_2TiCl_2 catalyst precursor is introduced which results from the reduction of titanium(IV). When the polymerization reaction begins, the ionic liquid phase becomes white and swells considerably as the polyethylene appears. At the same time, the hexane phase remains colourless and transparent. After 5–10 minutes, the hexane phase becomes a white suspension as the polyethylene is progressively shifted from the ionic liquid phase.

Alkylaluminum compound

Table 1 presents the influence of the kind of alkylaluminum compound on the yield of biphasic ethylene polymerization reaction. Regardless of the alkylaluminum compound applied, the polyethylene appears in a form of white powder. The best results were obtained using the activators containing chlorine atoms, such as AlEt_2Cl or AlEtCl_2 , but not MAO — the activator most frequently used for metallocene catalysts. The total PE yield increases with the polymerization time (Table 1, items 3 and 4), which indicates that the catalyst is stable. Increase in ethylene pressure, from 0.1 to 0.5 MPa, results in higher PE yield (Table 1, items 3 and 7). It should be noted that AlEtCl_2 , not investigated earlier, appeared to be the most effective activator (Table 1, items 9 and 10).

Table 1. Influence of the alkylaluminum compound on the yield of the ethylene polymerization using a titanocene catalyst (reaction conditions: $t_p = 30\text{ min}$, $T = 30\text{ }^\circ\text{C}$, $V_{\text{hexane}} = 150\text{ ml}$, $V_{\text{ionic liquid}} = 5\text{ ml}$, $\text{Ti} = 1.2 \cdot 10^{-4}\text{ mol}$, $\text{Al/Ti} = 17\text{ mol/mol}$)

Item	[cation] ⁺ [AlCl ₄] ⁻	Activator	PE yield (kg PE/mol Ti)		
			in ionic liquid	in hexane	total
<i>p</i> = 0.1 MPa					
1	EMIM	MAO	0.0	3.3	3.3
2	EMIM	AlEt_3	1.9	0.2	2.1
3	EMIM	AlEt_2Cl	2.7	0.7	3.4
4 ^{*)}	EMIM	AlEt_2Cl	4.1	2.1	6.2
5	EMIM	AlEtCl_2	3.4	0.8	4.2
6	BMIM	AlEtCl_2	8.7	0.1	8.8
<i>p</i> = 0.5 MPa					
7	EMIM	AlEt_2Cl	0.4	7.4	7.8
8 ^{*)}	EMIM	AlEt_2Cl	1.4	15.2	16.7
9 ^{*)}	BMIM	AlEtCl_2	22.6	28.0	50.6
10 ^{*)}	EMIM	AlEtCl_2	not separated	101.7	

^{*)} Polymerization time, $t_p = 60\text{ min}$.

Activator/catalyst (Al/Ti) molar ratio

Table 2 illustrates the influence of the activator/catalyst molar ratio, defined as Al/Ti molar ratio, on the yield of the biphasic ethylene polymerization. The two most active alkylaluminum compounds, AlEt_2Cl and AlEtCl_2 , were chosen as the activators. The investigations were performed for the following ionic liquid/activator combinations: $[\text{EMIM}]^+[\text{AlCl}_4]^-/\text{AlEt}_2\text{Cl}$, $[\text{EMIM}]^+[\text{AlCl}_4]^-/\text{AlEtCl}_2$, and $[\text{BMIM}]^+[\text{AlCl}_4]^-/\text{AlEtCl}_2$. The amount of the alkylaluminum compound was constant ($2 \cdot 10^{-3}\text{ mol}$), whereas the amount of Cp_2TiCl_2 was changed. For comparison, in this table also the results concerning the previously investigated system $[\text{BMIM}]^+[\text{AlCl}_4]^-/\text{AlEt}_2\text{Cl}$ are given [6].

When AlEt_2Cl is used as the activator and $[\text{EMIM}]^+[\text{AlCl}_4]^-$ as the ionic liquid, the increase in Al/Ti molar ratio from 17 to 33 results in two times

greater PE yield (Table 2, items 11 and 12). A further increase in Al/Ti molar ratio, up to 67, seems to be disadvantageous as it decreases the PE yield, similarly to our previous results obtained with use of [BMIM]⁺[AlCl₄]⁻ ionic liquid (Table 2, items 14 and 18). However, application of a twice greater volume of [EMIM]⁺[AlCl₄]⁻ does not result in a greater PE yield, whereas it does for [BMIM]⁺[AlCl₄]⁻ having a longer *n*-butyl substituent (Table 2, items 12, 13 and 16, 17).

Table 2. Influence of the activator/catalyst (Al/Ti) molar ratio on the yield of the biphasic ethylene polymerization using a titanocene catalyst with three modified ionic liquid systems (reaction conditions: $t_p = 60$ min, $T = 30$ °C, $p = 0.5$ MPa, $V_{hexane} = 150$ ml, $V_{ionic\ liquid} = 5$ ml, $Al = 2 \cdot 10^{-3}$ mol)

Item	Ionic liquid	Al/Ti molar ratio	PE yield (kg PE/mol Ti)		
			in ionic liquid	in hexane	total
AlEt ₂ Cl activator					
11		17	1.4	15.3	16.7
12	[EMIM] ⁺	33	2.8	29.3	32.2
13 ^{*)}	[AlCl ₄] ⁻	33	7.8	24.0	31.8
14		67	5.5	20.7	26.2
15 ^{**)}		17	3.0	23.3	26.3
16 ^{**)}	[BMIM] ⁺	33	6.0	20.7	26.7
17 ^{**)*)}	[AlCl ₄] ⁻	33	3.3	32.5	35.8
18 ^{**)*)}		67	1.7	18.0	19.7
AlEtCl ₂ activator					
19		17	not separated		101.7
20	[EMIM] ⁺	33	not separated		123.3
21	[AlCl ₄] ⁻	67	13.3	103.3	116.7
22		133	8.7	108.7	117.4
23		17	22.6	28.0	50.6
24		33	16.2	66.7	82.8
25		67	14.7	113.3	128.0
26 ^{*)}	[BMIM] ⁺	67	not separated		186.7
27	[AlCl ₄] ⁻	133	32.3	183.1	215.4
28 ^{**)*)}		133	53.0	307.0	360.0
29 ^{**)*)}		200	47.0	140.0	187.0

^{*)} A twice greater volume (10 mL) of the ionic liquid was applied.

^{**)} These results were published previously [6].

^{**)*)} A twice greater volume (300 mL) of the hexane phase was applied.

Application of AlEtCl₂ as an activator results in a much greater PE yield than when AlEt₂Cl is used, regardless of the ionic liquid type. In the case of [EMIM]⁺[AlCl₄]⁻ ionic liquid, the optimal Al/Ti molar ratio equals 67, although it is difficult to separate the phases (Table 2, items 19 and 20). In the case of [BMIM]⁺[AlCl₄]⁻, the PE yield increases up to the Al/Ti molar ratio value equal 267, when almost twice greater amount of polyethylene was obtained as compared to the use of [EMIM]⁺[AlCl₄]⁻ (Table 2, items 27 and 22). And even better yield, 360 kg PE/molTi, can be obtained by increasing twice the volume of hexane phase, which also makes far easier the separation of phases (Table 2,

item 28). A further increase in Al/Ti molar ratio results in a decrease in PE yield (Table 2, item 29).

The results obtained indicate that AlEtCl₂ is the best activator among those investigated so far in biphasic ionic liquid/hexane ethylene polymerization. Comparison of 1-ethyl- and 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate ionic liquids (Tables 1 and 2) shows that [BMIM]⁺[AlCl₄]⁻, having a longer substituent, is more suitable for biphasic ethylene polymerization. It should be noted that the PE yield increases with the increase in volume of both the ionic liquid and hexane phases. It can be concluded therefore, that a greater volume of both phases facilitates diffusion of ethylene molecules into the ionic liquid phase containing the active sites of the titanocene catalyst. On the other hand, it also facilitates the flow of polyethylene molecules from the ionic liquid into the hexane phase.

Catalyst leakage

It is very important to know how efficient the maintenance of the titanocene catalyst in the ionic liquid is and whether catalyst leakage occurs or not, which can result in the presence of the catalyst active sites in the hexane phase. To answer this question, the experiments were performed where the ionic liquid phase ([EMIM]⁺[AlCl₄]⁻ or [BMIM]⁺[AlCl₄]⁻) contained the Cp₂TiCl₂ catalyst and the alkylaluminum compound (AlEt₂Cl or AlEtCl₂) was mixed with hexane under a nitrogen atmosphere for one hour at 30 °C. After the layers had settled, the ionic liquid was discarded and the hexane phase was taken into the ethylene flush at typical polymerization conditions (0.5 MPa, 30 °C, 60 min). The hexane mixed over [BMIM]⁺[AlCl₄]⁻ remained transparent and no polyethylene was obtained. This means that the titanocene catalyst is efficiently anchored in the [BMIM]⁺[AlCl₄]⁻ ionic liquid. However, in the case of the hexane mixed over [EMIM]⁺[AlCl₄]⁻ a small amount of polyethylene was produced. This means that [EMIM]⁺[AlCl₄]⁻ is not as suitable carrier of the titanocene catalyst as [BMIM]⁺[AlCl₄]⁻ one.

Catalyst recycling

The presented biphasic ionic liquid/hexane ethylene polymerization experiments show that the Cp₂TiCl₂ catalyst can be immobilized in the ionic liquid phase, whereas the polyethylene produced flows into the hexane phase, which can then be easily separated. Thus, the catalyst and ionic liquid can be reused. Table 3 presents the three-cycle reaction processes using [EMIM]⁺[AlCl₄]⁻ and [BMIM]⁺[AlCl₄]⁻ ionic liquids as well as AlEt₂Cl and AlEtCl₂ activators, at the optimal activator/catalyst molar ratio. As can be seen, the greatest amount of PE was obtained during the first cycle. In order to perform further polymerization cycles, the ionic liquid phase must be saved and carefully separated,

Table 3. Catalyst recycling (reaction conditions: $t_p = 60$ min, $T = 30$ °C, $p = 0.5$ MPa, $V_{\text{hexane}} = 150$ ml, $V_{\text{ionic liquid}} = 5$ ml, $Al = 2 \cdot 10^{-3}$ mol)

Item	Activator	Al/Ti molar ratio	PE yield (kg PE/mol Ti)		
			in ionic liquid	in hexane	total
[BMIM] ⁺ [AlCl ₄] ⁻ ionic liquid					
30	AlEtCl ₂	133	2.7	160.0	160.0
31		133		53.3	53.3
32		133		23.3	26.0
				Σ	239.3
[EMIM] ⁺ [AlCl ₄] ⁻ ionic liquid					
33	AlEt ₂ Cl	33	2.8	27.5	27.5
34		33		4.8	4.8
35		33		1.6	4.4
				Σ	36.7
36	AlEtCl ₂	133	27.3	80.0	80.0
37		133		24.0	24.0
38		133		2.1	29.4
				Σ	133.4

what is a difficult process. Thus, the yield obtained during the first cycle is slightly lower than that obtained during standard polymerization procedure (see Table 2, item 27 and Table 3, item 30). A considerable loss of catalyst performance can be also observed in the second and third cycles. Nevertheless, the experiments show that it is possible to perform a multicycle biphasic polymerization process. The total amount of polyethylene obtained using catalyst recycling is greater than that obtained in a single step reaction (Tables 3 and 2), which can be a way to increase the catalyst performance.

Polyethylene properties

The presented results of investigations on the biphasic ethylene polymerization show that the majority of

polyethylene produced flows into the hexane phase. Nevertheless, some amount of polyethylene remains in the ionic liquid phase. Therefore, it is necessary to analyze the properties of both polyethylene fractions. The polyethylene obtained was washed with methanolic solution (see Experimental part) before it was subjected to DSC, GPC and FTIR analyses. Table 4 presents the selected polyethylene properties: melting point, crystallinity degree, molecular weight, molecular weight distribution (*MWD*), and number of methyl groups per 1000 methylene groups, which enables the evaluation of the linearity of polyethylene samples. The chosen PE samples were produced using [EMIM]⁺[AlCl₄]⁻ ionic liquid containing each of the applied alkylaluminum compounds as well as those obtained using [BMIM]⁺[AlCl₄]⁻ with AlEtCl₂, which were not analyzed previously.

The polyethylene samples collected from the hexane phase show high purity. A high degree of crystallinity (87–96 %) is another distinguishable physical feature of PE obtained. It should be noted that PE obtained with use of heterogeneous titanium catalyst supported on modified MgCl₂, showed much lower degree of crystallinity (55–68 %) [10]. This is important from a technological point of view, as a higher degree of crystallinity is related to better mechanical properties of plastics such as elasticity, impact strength, and abrasion resistance. Simultaneously some properties are deteriorated, such as transparency, chemical resistance and thermal expansion.

The PE from the hexane phase has molecular weight in the range 60 000–140 000 and a relatively narrow and monomodal *MWD* (4.1–4.6). The exception is the PE sample produced in the presence of MAO, which shows the broad bimodal character of *MWD* (Table 4, item 1).

The melting points are typical for low-pressure polyethylenes (130–134 °C). FTIR analysis shows that the number of CH₃ groups is in the range 3.7–13.3 per 1000 CH₂ groups, which is typical for linear polyethylene.

Table 4. Selected properties of the PE obtained using Cp₂TiCl₂ catalyst in biphasic ionic liquid/hexane polymerization

Item ^{*)}	Ionic liquid	Activator	Polyethylene:											
			hexane phase						ionic liquid phase					
			<i>Mp</i> °C	crystallinity degree %	<i>M_w</i> · 10 ⁻³	<i>MWD</i>	CH ₃ /1000 CH ₂	bulk density g/dm ³	<i>Mp</i> °C	crystallinity degree %	<i>M_w</i> · 10 ⁻³	<i>MWD</i>	CH ₃ /1000 CH ₂	bulk density g/dm ³
23	[BMIM] ⁺ [AlCl ₄] ⁻	AlEtCl ₂	132.4	94.9	—	—	9.6	260	129.8	95.6	—	—	23.2	—
24			134.0	86.7	—	—	3.7	243	133.3	93.4	—	—	4.2	236
28			132.5	94.2	103.8	4.1	7.5	222	129.8	90.1	14.1	5.3	15.9	180
29			131.2	95.7	93.6	4.4	13.3	208	128.2	88.4	12.8	3.9	29.9	186
1	[EMIM] ⁺ [AlCl ₄] ⁻	MAO	—	—	66.7	13.1	8.0	—	128.9	87.7	22.4	7.9	18.7	144
2		AlEt ₃	131.2	88.3	—	—	9.0	—	—	—	—	—	—	—
8		AlEt ₂ Cl	131.8	87.0	141.7	4.3	8.6	162	131.2	92.4	25.9	8.3	—	185
7		AlEt ₂ Cl	130.4	88.3	—	—	8.2	200	129.4	86.2	—	—	14.9	—
22		AlEtCl ₂	130.6	88.1	104.1	4.3	—	277	129.1	92.7	14.2	4.3	23.1	258
21		AlEtCl ₂	131.3	88.4	115.6	4.6	8.9	280	130.4	94.1	12.4	5.4	15.4	235

^{*)} Items numbered according to the experiments presented in Tables 1–3.

Interestingly, bulk density is relatively high (160—280 g/dm³).

The main difference between the polyethylene samples separated from hexane and ionic liquid phases is the much lower molecular weights of the latter ($M_W \sim 12\,000$ — $26\,000$). The melting points are also slightly lower (128—133 °C), similarly the bulk density (144—258 g/dm³). The numbers of CH₃ groups per 1000 CH₂ groups are greater (4—30), and MWDs are broader (3.9—8.3). In contrast, the crystallinity degree (88—95 %) is very similar for the samples collected from both phases.

It must be noted, however, that despite the samples purification, the color of polyethylene samples from the ionic liquid phase remain an off-white, pinkish. Also, FTIR analysis shows additional bands, which makes difficult the evaluation of the number of methyl groups. This indicates that PE samples from the ionic liquid phase still remain somehow contaminated. This can influence the credibility of the measurements of the physical properties.

Regardless of the kind of the ionic liquid applied, the PE samples obtained using AlEt₂Cl or AlEtCl₂ seem to be much cleaner and show better physical properties than those obtained using MAO or AlEt₃.

CONCLUSIONS

The biphasic ionic liquid/hexane ethylene polymerization, investigated herein, applies the ionic liquids — [EMIM]⁺[AlCl₄]⁻ or [BMIM]⁺[AlCl₄]⁻ — as a phase of the Cp₂TiCl₂ titanocene catalyst activated by alkylaluminum compounds such as MAO, AlEt₃, AlEt₂Cl or AlEtCl₂.

AlEtCl₂ appeared to be the best activator among those investigated so far in biphasic ionic liquid/hexane ethylene polymerization. This is the most effective activator, giving the greatest PE yield, regardless of the ionic liquid type and Al/Ti molar ratio used. The PE samples obtained using AlEtCl₂ as well as AlEt₂Cl seem to be much cleaner and show better physical properties than those obtained using MAO or AlEt₃.

The [BMIM]⁺[AlCl₄]⁻ ionic liquid is a better medium for the titanocene catalyst than [EMIM]⁺[AlCl₄]⁻ one. It

efficiently anchors the catalyst, in contrast to [EMIM]⁺[AlCl₄]⁻, for which a catalyst leakage was observed. Applied together with AlEtCl₂, it let reach the yield 360 kg PE/(mol Ti · h), which is a value comparable to the process with use of a heterogeneous metallocene catalyst supported on a solid carrier [11].

The multi-cycle biphasic polymerization process (catalyst recycling) is possible, what opens the way to a further increase in a catalyst performance.

The product obtained is characterized primarily by a high crystallinity degree and has the properties like a typical linear polyethylene.

All this together indicates that the application of metallocene catalysts in biphasic process with use of ionic liquid can be a potential alternative to their heterogenization on a solid carrier.

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