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Comparison of imidazolium and pyridinium ionic liquids as the media for biphasic ethylene polymerization in the presence of titanocene catalyst**)

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Summary — Tetrachloroaluminate ionic liquids having 1-*n*-octyl-3-methylpyridinium $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ or 1-*n*-octyl-4-methylpyridinium cation $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$, respectively, were investigated in the biphasic ionic liquid/hexane mode ethylene polymerization as media of bis(cyclopentadienyl)titanium(IV)dichloride (Cp_2TiCl_2) titanocene catalyst activated by $AlEtCl_2$ alkylaluminum compound. The results were compared to those obtained with using 1-*n*-octyl-3-methylimidazolium tetrachloroaluminate ionic liquid ($[C_8\text{-mim}]^+[AlCl_4]^-$). It was found that the pyridinium ionic liquids enable to obtain better polyethylene (PE) yields in total than the imidazolium ionic liquids. The best results were obtained using $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$, in which the alkyl substituents were in *para* (γ) positions at the pyridinium cation. The considerable amount of PE formed in the ionic liquid phase, largely contaminated, was observed at higher activator/catalyst (Al/Ti) molar ratio. It results from the mass transfer limitation through the phases. This obstacle disappears at lower activator/catalyst molar ratio and polyethylene produced is easily transported into the hexane phase. The effects of Al/Ti ratio and polymeryzation time on the total PE yield were also studied. PE obtained in the biphasic ionic liquid/hexane mode reveals molecular characteristics similar to polyethylenes produced in the presence of both homogeneous (low molecular weight) or heterogeneous (broad molecular weight distribution) metallocene catalyst systems. Additionally, it shows some unique features, such as high crystallinity degree and bulk density.

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

PORÓWNANIE IMIDAZOLIOWYCH I PIRYDYNIOWYCH CIECZY JONOWYCH JAKO ŚRODOWISK DWUFAZOWEJ POLIMERYZACJI ETYLENU PROWADZONEJ WOBEC KATALIZATORA TYTANOCENOWEGO

Streszczenie — Chloroglinianowe ciecze jonowe z kationem 1-*n*-oktylo-3-metylopirydyniowym $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ lub 1-*n*-oktylo-4-metylopirydyniowym $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$ zastosowano jako jedną z faz w dwufazowej polimeryzacji etylenu w układzie ciecz jonowa/heksan, prowadzonej wobec katalizatora tytanocenowego (Cp_2TiCl_2) aktywowanego $AlEtCl_2$. Wydajności polimeryzacji i właściwości polimerów otrzymanych z udziałem wymienionych cieczy jonowych porównano z odpowiednimi wielkościami uzyskanymi wcześniej przy udziale cieczy imidazoliowej ($[C_8\text{-mim}]^+[AlCl_4]^-$) (tabele 1 i 2). Stwierdzono, że wprowadzenie do układu pirydyniowych zamiast imidazoliowych cieczy jonowych skutkuje wzrostem całkowitej wydajności procesu, widocznym przede wszystkim w przypadku cieczy z kationem zawierającym podstawniki w pozycji para (γ) względem siebie. Jednakże wadą układów pirydyniowa ciecz jonowa/heksan był znaczny udział powstającego polietylenu (PE) w cieczy jonowej. Powoduje to wzrost stopnia jego zanieczyszczenia wynikający z utrudnionego przeniesienia masy przez granicę faz. Korzystny efekt przeniesienia niemal całej ilości powstającego polietylenu z fazy cieczy jonowej do fazy heksanowej występuje jedynie w warunkach małych wartości stosunków molowych aktywator/katalizator (Al/Ti). Zbadano także wpływ stosunku Al/Ti

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na ogólną wydajność PE. Charakterystyka wybranych właściwości polietylenu otrzymanego w układach dwufazowych tetrachloroglinianowa ciecz jonowa/heksan wykazała, że łączy on cechy polimeru uzyskanego wobec homogenicznych (mały ciężar cząsteczkowy) i heterogenicznych (szeroki rozkład ciężarów cząsteczkowych, duża gęstość nasypowa) układów metalocenowych. Ponadto charakteryzuje go nietypowy dla PE, bardzo wysoki stopień krystaliczności, zwłaszcza w przypadku zastosowania cieczy pirydyniowych (> 90 %).

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

IONIC LIQUIDS — GENERAL CHARACTERIZATION

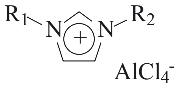
Homogeneous catalyst systems applied in majority of the organic reactions are commonly afflicted by difficulties such us separation of the products from reaction mixture, lack of re-use of catalyst, and necessity of application of volatile organic solvents [1, 2].

These disadvantages can be potentially reduced by the biphasic liquid/liquid catalysis, which constantly attract considerably attention. The biphasic system has numerous technological and ecological advantages. It makes possible high catalyst activities, moderate reaction conditions, easy product separation, and catalyst recycling [1, 3]. Recently, particular attention has been devoted to biphasic systems, in which one phase constitutes a ionic liquid.

The ionic liquids are perceived as an alternative to the use of common volatile organic solvents. Negligible volatility, liquid state in a wide range of temperature, chemical and thermal stability, polar but weakly coordinating character, make the ionic liquids attractive reaction media. The ionic liquids are good solvents for numerous organic, inorganic, and organometallic compounds, but on the other hand, they have limited miscibility with organic solvents. This feature makes possible to apply the ionic liquids in the biphasic systems [4—11].

An important factor, which rises the popularity of the ionic liquids is a possibility to control their physical and chemical properties by changing the combination of cations and anions. For example, melting point, density, viscosity, hydrophobicity, thermal stability, and surface tension can be tuned in this manner, as it was shown in the investigation of 1-*n*-alkyl-3-methylimidazolium ionic liquids by changing the alkyl side chains at the imidazolium ring [4, 12—14].

In our previous studies, a series of 1-*n*-alkyl-3--methylimidazolium tetrachloroaluminates (where alkyl = ethyl, butyl, hexyl, or octyl) [Formula (I)] was applied as a phase in biphasic ethylene polymerization [15—17].

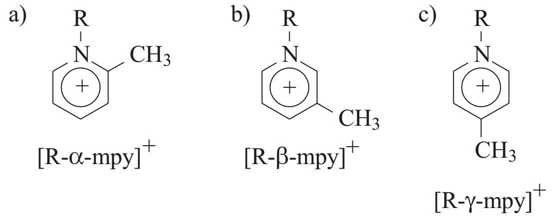


(I)

The ionic liquid was a medium of Cp_2TiCl_2 titanocene catalyst and alkylaluminum activator. Polyethylene produced in the ionic liquid phase was transferred to the hexane phase. This biphasic ionic liquid/hexane system made possible to separate easily PE product from the reaction mixture what resulted in its considerable high purity. Immobilization of the catalyst in the ionic liquid phase and the lack of its leakage were confirmed experimentally. Thus, it was possible to re-use the catalyst in consecutive polymerization reactions. Traditional alkylaluminum compounds were used as activators of metallocene catalyst instead of methylalumoxane (MAO).

It was also found that the kind of alkyl substituent at the imidazolium cation of the ionic liquid influenced the performance of the polymerization reaction and the properties of PE produced. The change of the physical properties related to the character of the ionic liquid cation made possible to control the polymerization reaction course and to design the properties of PE product [17].

The promising results obtained with use of tetrachloroaluminate ionic liquid with 1-*n*-octyl-3-methylimidazolium cation ($[C_8\text{-mim}]^+[AlCl_4]^-$) encouraged us to investigate the pyridinium ionic liquids. It should be noticed that the properties of the dialkylpyridinium cation [Formula (2)] could be designed not only by the change of the type but also the position of the alkyl substituent at the pyridinium ring.



(II)

The pyridinium ionic liquid was not yet investigated in the olefin polymerization. The scarce literature reports concern the application of the pyridinium ionic liquids in dimerization [18, 19] and olefin oligomerization reactions [20]. They were applied mainly in other types of the organic syntheses, *e.g.*, Heck, Diels-Alder, Friedel--Crafts, as well as Beckman rearrangement reactions [9, 21—23].

EXPERIMENTAL

Materials

— Ethylene (Linde AG Gaz) and pure nitrogen (Messer) were used after passing through a column with sodium metal supported on Al_2O_3.

— Hexane (POCH, Gliwice) was refined with sulfuric acid 95 % (POCH, Gliwice), dried with sodium hydroxide, distilled in the temperature range 60—70 °C, and stored over 4A molecular sieves.

— Substrates for the ionic liquids syntheses: 2-methylpyridine (C_6H_7N, Fluka), 3-methylpyridine (C_6H_7N, Fluka), 1-methylimidazole ($C_5H_6N_2$, Fluka), and 1-chlorooctane ($C_8H_{17}Cl$, Fluka) were applied as purchased.

— Catalyst — bis(cyclopentadienyl)titanium(IV) dichloride (Cp_2TiCl_2, Aldrich) and activator — ethylaluminium dichloride ($AlEtCl_2$, Aldrich) (1M as hexane solution), were applied as purchased.

— HCl 35—38 wt. % (POCH, Gliwice), ethyl acetate and methanol (POCH, Gliwice) were applied a purchased.

— Diethyl eter [$(C_2H_5)_2O$, POCH, Gliwice] was distilled from the sodium metal.

Ionic liquid syntheses

The ionic liquids syntheses were performed as described previously [17]. The yields of the syntheses were as following: 35 % and 52 % for $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$, and 80 % for $[C_8\text{-mim}]^+[AlCl_4]^-$, respectively.

Biphasic ethylene polymerization

All steps were carried out in oxygen-free conditions using an inert nitrogen atmosphere.

The biphasic polymerization reaction was conducted in a 500 ml glass reactor equipped with a mechanical stirrer and a water jacket to maintain a constant temperature. In the biphasic system applied, the bottom phase was constituted by the ionic liquid, in which the catalyst and activator were dissolved. The upper phase was hexane (150 ml) with addition of activator (2×10^{-4} mol of Al) acting as a scavenger of impurities [15, 16]. It was a place where PE produced was gathered.

The ionic liquid (5 ml) phase was mixed with $AlEtCl_2$ (alkylaluminum activator) (1.0×10^{-3} — 6.0×10^{-3} mole) and stirred for 24 hours. Shortly before the polymerization reaction begin, the constant amount of Cp_2TiCl_2 catalyst (3.0×10^{-5} mol) was added to the previously prepared ionic liquid/activator mixture. The hexane and the ionic liquid phases were added successively into the reactor.

The polymerization reaction was initiated by ethylene feeding, bubbled through the ionic liquid phase, and carried out at constant pressure (0.5 MPa) and temperature (30 °C).

To terminate the polymerization reaction after 60 min or 120 min, ethylene feeding was closed and both hexane and ionic liquid phases were separated by decantation. Solution of hydrochloric acid in methanol (5 wt. %) was added to each phase. PE obtained, in form of a powder — white and off-white for hexane and ionic liquid phases, respectively — was filtered off, washed with methanol and dried at room temperature.

Methods of testing

— The ionic liquid analysis was performed based on the FTIR, ^{1}H NMR, and ^{13}C NMR spectra. The FTIR analysis was carried out using a Philips Analytical PU 9800 spectrometer (resolution $R = 2$ cm^{-1}, bands 4000 — 400 cm^{-1}, in Nujol KBr/KBr). The NMR spectra of the ionic liquids samples were recorded using a Bruker Ultrashield spectrometer (400 MHz).

— Molecular weights and molecular weight distributions (*MWD*) of PE samples 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.

— Crystallinity degree (*C*) and melting temperature (T_m) of PE samples were estimated using a DSC 2010 TA Instruments Differential Scanning Calorimeter. The *C* value was calculated using the equation:

$$C\ (\%) = (\Delta h_f / \Delta h_s) \times 100\ \% \tag{1}$$

where: Δh_f — *heat of fusion of polyethylene sample*, Δh_s — *heat of fusion of standard (290 J/g).*

— Bulk density of polyethylene was determined according to ASTM Standard D 1895.

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

RESULTS AND DISCUSSION

Influence of the kind of ionic liquid on the performance of ethylene polymerization

The previous studies of 1-*n*-alkyl-3-methylimidazolium tetrachloroaluminate ionic liquids as the media for Cp_2TiCl_2 titanocene catalyst proved that ethylene polymerization carried out in a biphasic ionic liquid/hexane mode was possible [15—17]. It was found that $[C_8\text{-mim}]^+[AlCl_4]^-$ ionic liquid having the longest (octyl) alkyl substituent at the imidazolium cation gave the best performance of ethylene polymerization, *i.e.* satisfactory yield with majority of PE product in the hexane phase (Table 1, items 1—7) [17]. Therefore, the pyridinium ionic liquid with the octyl substituent was chosen as the subject of investigation of the biphasic ethylene polymerization. Additionally, as was mentioned before, it was interesting to evaluate how the positions of two alkyl substituents at the pyridinium cation, each to other, influenced the performance of ethylene polymerization. In a consequence, two pyridinium ionic liquids were selected for this study, namely $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$. The polymerization was carried out in the conditions elaborated previously for the imidazolium ionic liquids [15]. As an activator, $AlEtCl_2$ was applied, which was found to be the best for the biphasic ionic liquid/hexane polymerization [16, 17].

Table 1. Influence of the kind of the ionic liquid and the activator ($AlEtCl_2$)/catalyst (Cp_2TiCl_2) molar ratio (Al:Ti) on PE yield in the biphasic ionic liquid/hexane mode of polymerization; polymerization time 60 min or (*) 120 min

No	Ionic liquid	Al/Ti molar ratio	PE yield (kg PE/mol Ti)		
			ionic liquid phase	hexane phase	total
1	$[C_8\text{-mim}]^+[AlCl_4]^-$	33	–	–	–
2		67	10.7	46.7	57.3
3		100	14.4	62.0	76.4
4		133	17.0	101.0	118.0
5		167	78.0	85.7	163.7
6*)		100	13.7	146.7	160.3
7*)		133	48.3	147.0	195.3
8	$[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$	33	–	–	–
9		67	8.0	68.0	76.0
10		100	76.7	36.7	113.3
11		133	101.7	41.0	142.7
12*)		67	65.7	37.67	103.3
13*)		133	103.3	105.0	208.3
14	$[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$	33	–	–	–
15		67	5.3	59.8	65.1
16		100	94.3	42.0	136.3
17		133	171.5	37.5	209.0
18*)		67	8.9	81.1	90.1
19*)		133	42.0	236.7	278.7

The experiments showed that PE product, in the form of white powder, was present not only in the hexane phase but also remained in the ionic liquid phase. At the beginning of the polymerization reaction the ionic liquid phase whitens and swells considerably as polyethylene appears, whereas hexane phase remains colourless and transparent — similarly, as it was in the case of imidazolium ionic liquids. After 5—10 minutes, the progressive transfer of PE product into the hexane phase becomes visible. This shows that the ethylene polymerization takes place in the ionic liquid phase.

The maintenance of the catalyst system in one phase is very important for biphasic catalysis mode. Therefore, it was proved, according to the method applied for the imidazolium ionic liquids [16], that Cp_2TiCl_2 titanocene catalyst dissolved in the pyridinium ionic liquids was not extracted by the hexane phase. It was immobilized completely in the ionic liquid phase and no catalyst leakage was observed.

In our previous investigations, 1-*n*-alkyl-3-methylimidazolium tetrachloroaluminate ionic liquids were applied in the biphasic ethylene polymerization [17]. It was found that for each ionic liquid studied, there was an optimal activator/catalyst molar ratio (Al/Ti), in which the yield obtained from the hexane phase was the highest. Further increase in Al/Ti molar ratio results in an increase in the total reaction yield, mainly due to disadvantageous increase in the amount of PE in the ionic liquid phase (Table 1, item 5). This ratio depends on the kind of the alkyl substituent at the imidazolium cation of the ionic liquid. The best results were obtained with use of 1-*n*-octyl-3-methylimidazolium tetrachloroaluminate ionic liquids $[C_8\text{-mim}]^+[AlCl_4]^-$, for which optimal Al/Ti molar ratio was 133 (Table 1, item 4).

In the case of pyridinium ionic liquids, in the studied range of the activator/catalyst molar ratio, solely the increase in PE yield was observed (Table 1, items 8—11, 14—17). As in the case of $[C_8\text{-mim}]^+[AlCl_4]^-$, for the studied $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$ pyridinium ionic liquids the lowest activator/catalyst molar ratio (Al/Ti = 33) was found too small to initiate the polymerization reaction (Table 1, items 1, 8, 14).

In the biphasic systems where the pyridinium ionic liquids were applied, PE yields were higher that those with use of imidazolium ionic liquid analogue (Table 1, items 2—4, 9—11, 15—17). There were also found the differences in the performance of the pyridinium ionic liquids used. The amount of PE produced was larger when $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$ was used (Table 1, items 9 and 15, 10 and 16, 11 and 17). It means that the pyridinium ionic liquid with the alkyl substituent at the *para* (gamma) position is favoured in the biphasic ethylene polymerization reaction.

It should be also noticed that for both pyridinium ionic liquids, the relatively low amount of the activator (Al/Ti = 67) results in higher PE yield (both total as well as from the hexane phase) than when the analogous $[C_8\text{-mim}]^+[AlCl_4]^-$ ionic liquid was used (Table 1, items 2, 9, 15). The increase in the activator/catalyst molar ratio results in disadvantageous maintenance of PE product in the ionic liquid phase, although the total yield increases (Table 1, items 3—4 and 10—11, 16—17). It means that the application of the larger amount of $AlEtCl_2$ activator has disadvantageous impact on the polymer transfer to the hexane phase.

It is known that the length of alkyl substituent influences the physical properties of the ionic liquid such as density and viscosity [4, 13]. The longer alkyl substituent the lower density of the ionic liquid. The studied ionic liquids ($[C_8\text{-mim}]^+[AlCl_4]^-$, $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$, and $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$) have relatively low densities [4, 9]. This improves the contact between the ionic liquid and hexane phases and makes much easier the access of the monomer molecules to the active sites. However, the ionic liquid of low density makes separation from the hexane phase more difficult [17].

At low concentration of the activator the number of the active sites is relatively small, the amount of PE produced is smaller, and it is easily transferred to the hexane phase. At higher concentration of $AlEtCl_2$, the greater number of the active sites is created, the greater amount of PE is produced, the possibility of the system to transfer all the PE product to the hexane phase is exceeded, and thus, it remains in the ionic liquid phase.

It was found that prolongation of the reaction time improved substantially the total PE yield regardless of the kind of the ionic liquid and the concentration of the activator (Table 1, items 3 and 6, 4 and 7, 9 and 12, 11 and 13, 15 and 18, 17 and 19). Therefore, prolongation of the reaction time can be the way to increase the overall performance of the biphasic polymerization.

Influence of the kind of the ionic liquid on the polyethylene properties

The main idea of the application of the biphasic catalysis in ethylene polymerization is to maintain the titanocene catalyst in the ionic liquid phase, and simultaneously, to transfer PE produced to the hexane phase. As a result, the polymer showing high purity can be obtained. Some amount of polyethylene remains, however, in the ionic liquid phase and it is contaminated by the decomposition products of the catalyst, activator and ionic liquid. So, only the properties of PE from hexane phase were determined and presented in Table 2.

Table 2. Selected properties of PE obtained from the hexane phase, in the presence of Cp_2TiCl_2 catalyst in the biphasic ionic liquid/hexane mode of polymerization

No*)	Ionic liquid	PE properties					
		T_p °C	crystalinity degree %	bulk density g/dm^3	$M_w \cdot 10^{-3}$ g/mol	*MWD*	N**)
2	$[C_8\text{-mim}]^+[AlCl_4]^-$	136	89	–	165.6	7.2	–
3		135	88	340	129.2	6.8	6.15
4		133	88	480	69.8	5.8	9.57
6		133	87	530	212.6	6.7	8.20
9	$[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$	128	96	481	141.3	3.4	5.03
10		128	98	457	138.2	2.9	6.03
11		127	98	–	111.5	3.1	8.08
12		128	91	443	171.1	4.6	7.22
13		127	96	490	141.2	2.7	–
15	$[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$	133	96	208	132.2	4.8	4.43
16		133	95	395	110.4	5.1	5.31
18		134	93	368	154.1	6.2	4.17

*) Items according to Table 1.

**) Number of methyl groups (CH_3) per 1000 methylene groups (CH_2).

As can be seen, the melting points of PE obtained with use of $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$ and the imidazolium analogue are almost the same (Table 2, items 15, 16, 18 and 2—4, 6) (133 °C—135 °C) and similar for PE-HD [24], whereas are lower for PE samples obtained with use of $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ (~127.5 °C) (Table 2, items 9—13). In contrast, the bulk densities of PE obtained with use of $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and $[C_8\text{-mim}]^+[AlCl_4]^-$ are located in similar rauge, whereas it is lower for PE obtained with use of $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$. It should be noticed that such high values of bulk density of the polymer could be obtained only when heterogeneous metallocene catalysts were used. For the polymer obtained in the presence of homogeneous metallocene catalysts, the bulk density does not exceed the value of 100 g/dm^3 [25, 26].

A distinguish property of PE obtained with use of both pyridinium ionic liquids is very high crystallinity degree (~96 % for $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and ~95 % for $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$), much higher than those obtained with use of imidazolium ionic liquids (~88 %).

PE obtained with use of pyridinium ionic liquid has linear character and the number of branches of the main chain is similar (~6.6 and ~4.6 CH_3/1000 CH_2 for $[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$, respectively).

Despite of the high values of crystallity degree and bulk density and regardless of the kind of the ionic liquid studied, PE reveals relatively low molecular weight (M_w) in the range ~ 70 000 — 200 000 decreasing with an increase in activator/catalyst molar ratio (Table 2, items 2—4, 9—11, 15 and 16). It indicates an increase in the chain transfer reaction. The molecular weight distribution is relatively broad (*MWD* values from 2.9 to 6.2), which is typical rather for the polymer product obtained in the presence of supported metallocene catalyst [27—29].

On the basis of the presented results it can be concluded that the structure of the ionic liquid cation, including the position of the alkyl substituents at the pyridinium ring, has an influence on the performance of the polymerization reaction and consequently on PE yield and properties.

CONCLUSIONS

The presented studies confirmed the possibility of the application of the pyridinium ionic liquids ($[C_8\text{-}\beta\text{-mpy}]^+[AlCl_4]^-$ and $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$) as the media for Cp_2TiCl_2 titanocene catalyst activated by $AlEtCl_2$ in the biphasic ethylene polymerization. The structure of the ionic liquid cation influences the performance of the polymerization reaction. The pyridinium ionic liquids, particularly $[C_8\text{-}\gamma\text{-mpy}]^+[AlCl_4]^-$, make possible to obtain better PE yield in total than in case of imidazolium analogue. A disadvantageous feature of the pyridinium ionic liquid/hexane biphasic systems is that PE product remains in the ionic liquid phase at higher activator/catalyst molar ratio. It results from limited mass transfer between the ionic liquid and hexane phases. However, at lower activator/catalyst molar ratio the transfer of PE product to the hexane phase is greater than in the case of imidazolium ionic liquids, which is very important for biphasic polymerization process.

Polyethylene obtained in the presence of titanocene catalyst in the biphasic system, with use of the studied ionic liquids, reveals the properties characteristic for the products obtained in the presence of either homogeneous (*e.g.* low molecular weights) or heterogeneous (*e.g.* broad *MWD*s, high bulk densities) metallocene catalysts. The PE produced has very high crystallinity degree, which indicates high degree of macromolecular order and good mechanical properties of the polymer.

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