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Ionic Liquids in Biphasic Ethylene Polymerisation

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1. Introduction

Over the past several years there has been a considerable increase in the interest of ionic liquids as versatile reaction media for a wide variety of synthetic processes. The popularity of ionic liquids has been related primarily to their unique physical and chemical properties, which can be tailored by the judicious selection of cations and anions. These properties make it possible to use ionic liquids as solvents for many organic, inorganic, and organometallic compounds, including catalysts and co-catalysts, for various types of reactions. In particular, the polar but weakly coordinating character of ionic liquids enables them to be applied as mediums in catalysis, to immobilize various kinds of catalyst precursors which contain transition metals. Recently, ionic liquids have also been viewed as a “green” replacement to conventional organic solvents (Olivier-Bourbigou, 2002; Wasserscheid et al., 2004; Wilkes, 2004; Welton, 2004; Kubisa, 2004; Jain, 2005; Parvulescu et al., 2007; Chowdhury et al., 2007; Ochędzan-Siodłak, 2009).

Amongst many reactions carried out in an ionic liquids environment, dimerisation and oligomerisation reactions catalyzed by nickel complexes should be noted. In the majority of cases, an improvement in the activity and selectivity of the processes as well as the limitation of undesirable side reactions were achieved. Due to the good solubility of transition metal compounds in the ionic liquid phase, and simultaneously, a poor miscibility of the produced olefins, the reaction is commonly performed in a biphasic mode. The product creates a separate phase over the ionic liquid phase containing the dissolved catalyst. Thus, it becomes possible to easily separate the product from the reaction mixture, to minimize the waste of the expensive transition metal compound, and to use the catalyst repeatedly (recycling) (Chauvin et al., 1990; 1995; 1997; Einloft et al. 1996; Simon et al., 1998; Ellis et al., 1999; Pinheiro et al., 2001; Wasserscheid et al., 2001; Bernando-Gusmão et al., 2003; Wasserscheid et al., 2004).

The successful application of ionic liquids in the oligomerisation of 1-olefins inspired us to investigate the biphasic technique in polymerisation reactions using metallocene catalysts, which constitute the next generation of organometallic catalysts for olefin polymerization. Metallocenes in the past gained a considerable interest due to their high activities - up to several tons of the polymer product per gram of the transition metal. Unfortunately, it was found that such high activities can only be obtained for homogenous catalyst systems dissolved in carcinogenic solvents and activated by a great excess of expensive methylaluminoxane (MAO). Furthermore, the homogenous systems reveal low stabilities

during the polymerisation reactions, reaction fouling, and a lack of control of the polymer morphology (Kaminsky, Laban, 2001; Ewen, 2000).

To overcome these undesirable features, the metallocene systems were subjected to an anchorage on a solid carrier, for example SiO_2 , Al_2O_3 , MgCl_2 , as well as polymer compounds. The obtained heterogenisation of the metallocene systems makes it possible to control the product morphology, as well as resulting in an absence of reactor fouling, and a decrease in the amount of the MAO activator required. Unfortunately, the anchorage of the catalyst to the solid carrier results in a decrease of the activity (10-60%) as compared to the homogeneous analogue. The heterogenisation process is technically difficult to proceed, time consuming, and the polymer product reveals a considerable degree of inhomogeneity (Chen, 2000; Hlatky, 2000; Severn et al., 2005; Ochędzan-Siodłak, Nowakowska, 2005).

Therefore, there is a need to search for new, non-conventional performance methods of olefin polymerisation using metallocene catalysts. It seems that the immobilization of the metallocene catalyst in ionic liquids could be a potential alternative to its heterogenisation on a solid carrier.

2. Ethylene polymerisation

The ethylene polymerisation performed using the $[\text{C}_2\text{-mim}][\text{AlCl}_4]$ ionic liquid as a medium of the TiCl_4 catalyst activated by the AlEtCl_2 alkylaluminium compound was described for the first time by Carlin and Osteryoung. The polymerisation was carried out in the single phase mode (in the ionic liquid). Although only small amounts of the polyethylene product were obtained ($0.23 \text{ kgPE}/(\text{molTi} \cdot 10 \text{ min})$), the results indicated that ionic liquids can be applied to olefin polymerisation (Carlin et al., 1990). It was further found that amongst the Cp_2MCl_2 metallocene catalysts ($\text{M} = \text{Ti}, \text{Hf}, \text{Zr}$) activated by the $\text{AlCl}_3\text{-}x\text{R}_x$ alkylaluminium compounds ($\text{R} = \text{Me}, \text{Et}$), only the titanocene catalyst turned out to be active (Carlin, Wilkes, 1990).

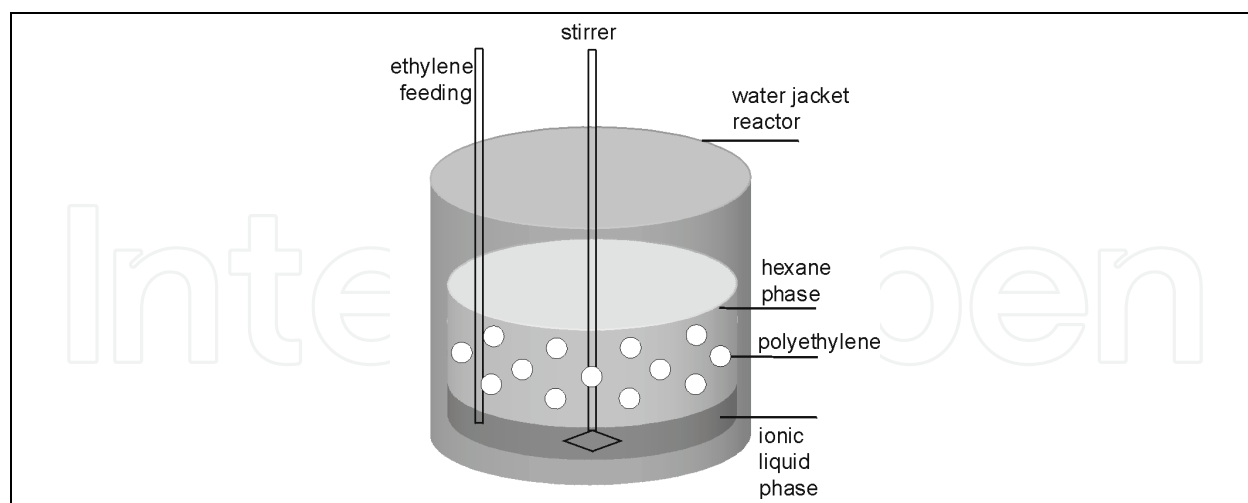


Fig. 1. The schematic representation of the studied biphasic ionic liquid/hexane polymerisation.

In our work, the polymerisation reaction was performed in the biphasic mode (Figure 1). The polymerisation of the simplest olefin, ethylene, was investigated as a model. The lower phase consisted of the ionic liquid, in which the Cp_2TiCl_2 catalyst and the alkylaluminium activators were dissolved. Hexane constituted the upper phase. For the ionic liquids, 1-*n*-

alkyl-3-methylimidazolium and 1-*n*-alkyl-4-methylpyridinium chloroaluminates substituted by alkyl chains of various length (*n* = butyl, hexyl, octyl) were applied (Ochędzan-Siodłak et al., 2007; 2008; 2009).

2.1 Biphasic process

For all biphasic ionic liquid/hexane polymerisation experiments performed, the following facts have been observed. Two phases, hexane and ionic liquid, are clearly visible from the beginning to the end of the reaction. At the beginning of the reaction 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 transferred from the ionic liquid phase. The polyethylene is obtained in form of a powder. It is white when obtained from the hexane phase and off-white when obtained from the ionic liquid phase. The polyethylene from the hexane phase can be easily isolated and subjected to analysis.

It is very important for the biphasic catalytic process to maintain the catalyst in the selected phase. This has been shown by experiments where the ionic liquid phase contained the Cp_2TiCl_2 catalyst and the alkylaluminium compound was washed with hexane. Catalyst leakage was not detected, which indicates that the titanocene is firmly immobilised in the ionic liquid phase and remains during the entire duration of the polymerisation (Ochędzan-Siodłak, Pawelska, 2008).

During the course of the polymerisation reaction, the polyethylene is progressively transferred to the hexane phase. At the same time, the amount of polyethylene in the ionic liquid phase decreases, however, the total polyethylene yield increases with the polymerisation time (Figure 2). This confirms that the polymerisation reaction takes place in the ionic liquid phase. It also indicates that the catalyst is stable.

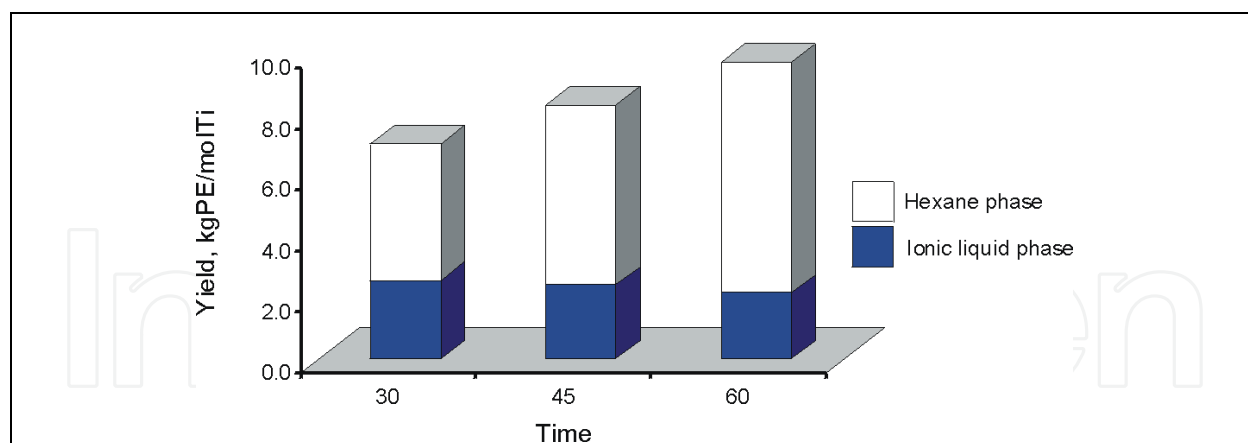


Fig. 2. The influence of the reaction time on the PE yield in the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquid - $[\text{C}_4\text{-mim}][\text{AlCl}_4]$, catalyst - Cp_2TiCl_2 , activator - AlEt_2Cl , $\text{Al}/\text{Ti} = 33$, standard pressure, room temperature.

The stability of the catalyst was also proved by the re-use of the ionic liquid phase containing the catalyst and the activators in the consecutive polymerisation reactions (Figure 3). The experiments consisted of three cycles, which were successfully performed, although the polymerisation yield gradually decreased. The catalyst was maintained in the ionic liquid phase whereas the polyethylene product was removed after each cycle with the

hexane phase. Thus, catalyst recycling is possible. Also, it seems to be a very important way to increase catalyst performance in the biphasic processes (Ochędzan-Siodłak et al., 2008).

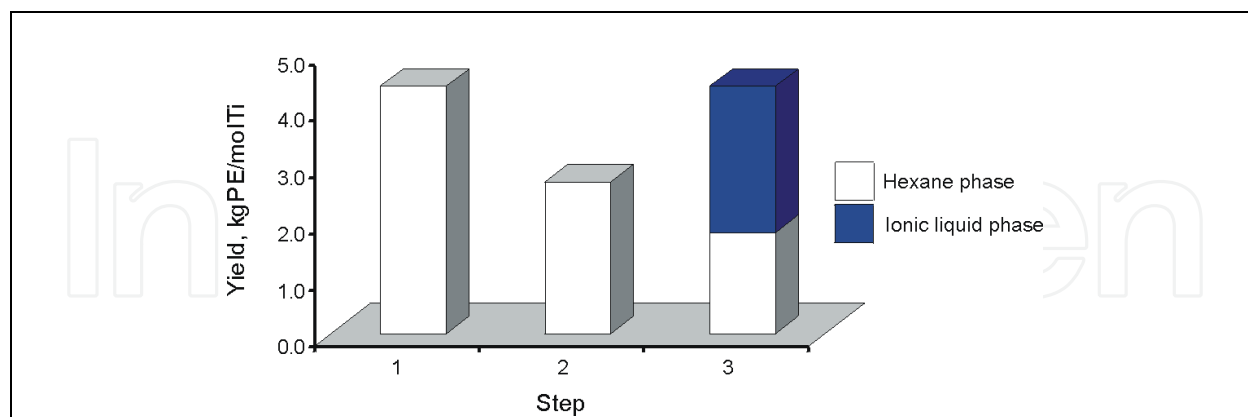


Fig. 3. The 3-step catalyst recycling in the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquid – $[C_4\text{-mim}][AlCl_4]$, catalyst – Cp_2TiCl_2 , activator – $AlEt_2Cl$, $Al/Ti = 33$, standard pressure, room temperature, reaction time – 30 min.

The results presented show that the application of the ionic liquid as a medium of the titanocene catalyst as well as the performance of the polymerisation reaction in the biphasic mode offer the following advantages; the polymer product can be easily separated from the reaction mixture using a simple decantation technique; the product is characterised by high purity; the product is transferred to the hexane phase, whereas the catalyst and activator remain in the ionic liquid phase. In addition, the catalyst presented in the ionic liquid phase is stable and catalyst leakage is not observed. Thus, recycling of both the catalyst and the ionic liquid is possible. It should be also noted that reaction fouling (common for the metallocene/MAO systems) is not present (Ochędzan-Siodłak et al, 2007; 2008).

2.2 Activators

The great advantage of ionic liquids over classic solvent is the fact that their properties can be tailored by the choice of suitable cations and anions. Applying a titanocene catalyst to the ethylene polymerisation limits the choice to the chloroaluminate ionic liquids because so far it is only this anion which makes the use of the alkylaluminium compounds as necessary catalyst activators possible. It should be noted that introduction of the alkylaluminium compound inevitably influences the anionic part of the ionic liquid. The kind and the amount of the alkylaluminium compound used are important because a range of mixtures of the chloroaluminate anions can be created. Also, the Lewis acidity of the ionic liquid is changed. This has considerable influence on the course and the performance of the ethylene polymerisation carried out in the biphasic mode.

The following alkylaluminium compounds: $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$, and MAO were investigated as activators of the Cp_2TiCl_2 catalyst (Figure 4). The best results were obtained for the compounds containing the chlorine atom, $AlEtCl_2$ and $AlEt_2Cl$. The more chlorine atom the activator contains, the higher the total yield, with the greater amount of polyethylene product transferred to the hexane phase. Interestingly, the worst results were obtained using methylaluminoxane (MAO), which is the best activator for the homogeneous metallocene catalysts. Therefore, the application of the ionic liquid to the ethylene polymerisation eliminates the need for the expensive MAO as the activator, which can be

superseded by traditional, cheaper alkylaluminium compounds (Ochędzan-Siodłak et al., 2007; 2008).

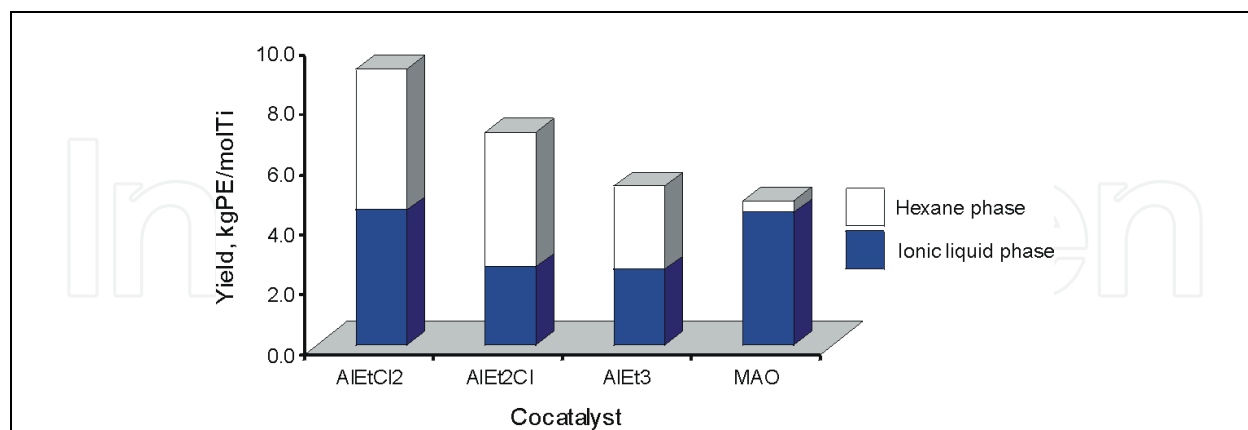


Fig. 4. The influence of various kinds of alkylaluminium activators on the performance of the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquid – $[C_4\text{-mim}][AlCl_4]$, catalyst – Cp_2TiCl_2 , Al/Ti = 33, standard pressure, room temperature, reaction time – 30 min.

2.3 Imidazolium ionic liquids

The further investigations focused mainly on the modification of the cationic part of the ionic liquid. Substituting the imidazolium and pyridinium cations by alkyl chains of various lengths makes it possible to tailor some of the physical properties of the ionic liquids. The two most effective activators, $AlEtCl_2$ and $AlEt_2Cl$, were applied (Ochędzan-Siodłak et al., 2007; 2008; 2009). The study performed using 1-*n*-alkyl-3-methylimidazolium ionic liquids, $[C_n\text{-mim}][AlCl_4]$, show that the length of the alkyl chain at the ionic liquid cation and the concentration of the alkylaluminium compound influence the performance of the biphasic polymerisation reaction, i.e. the total polymerisation yield, the amount of the polyethylene product gathered in the hexane phase, and the phase separation (Figure 5). For each studied ionic liquid, there is an optimal concentration of the alkylaluminium compound, in which the yield of the reaction is the highest and the majority of the product transfers to the hexane phase. For $[C_4\text{-mim}][AlCl_4]$ and $[C_6\text{-mim}][AlCl_4]$, ionic liquids with shorter alkyl chains, the activator/catalyst molar ratio (Al/Ti) reaches optimum at the value 100. A higher ratio results in a decrease of the yield and the majority of the product remains in the ionic liquid phase. For $[C_8\text{-mim}][AlCl_4]$, the ionic liquid with a longer alkyl chain, the optimal activator/catalyst molar ratio is higher (Al/Ti = 133) resulting in a total PE yield 120 kgPE/molTi·h. An even higher yield can be obtained at the activator/catalyst molar ratios 167 and 200. However, the majority of the product remains in the ionic liquid phase, which is disadvantageous to the biphasic process. Therefore, if two criteria for the performance of the biphasic process are the amount of the product gathered in the hexane phase and the ratio between the amount of product in both phases, the ionic liquid with the longest alkyl chain is the better medium for the titanocene catalyst as it results in the greatest amount of the pure polymer product from the hexane phase. It was also found that prolongation of the reaction time (up to 120 min.) improves the reaction yield. This confirms the stability of the catalyst immobilised in the ionic liquid and makes it possible to obtain the greatest amount of the product from the hexane phase.

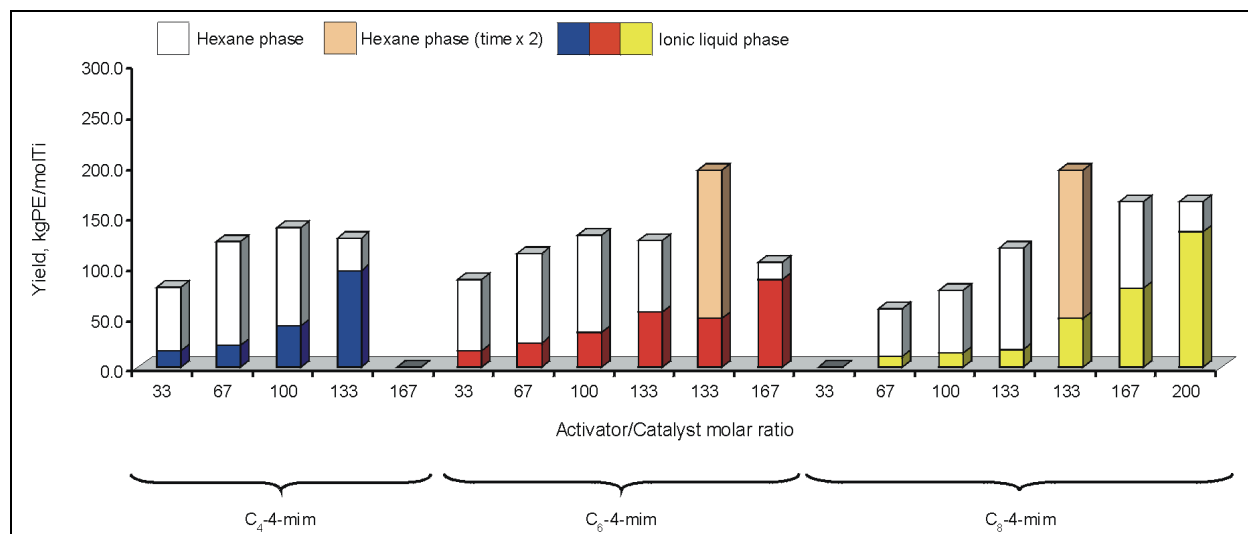


Fig. 5. The influence of the alkyl chain at the cation of the ionic liquids and the concentration of the AlEtCl₂ alkylaluminium activator on the performance of the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquid - [C_n-mim][AlCl₄] (n = 4,6,8), catalyst - Cp₂TiCl₂, activator - AlEtCl₂, pressure - 0.5MPa, room temperature, reaction time - 60 min.

When the AlEt₂Cl compound is used instead of AlEtCl₂, similar results were obtained (Figure 6). The yield increases with the increase of the concentration of the alkylaluminium compound. For the ionic liquids with shorter alkyl chains, the best results are obtained at the lower activator/catalyst molar ratio, whereas for the ionic liquid with the longer alkyl chain, a higher activator/catalyst molar ratio is required. However, the obtained yield is considerably lower, which indicates that the AlEt₂Cl compound is not as efficient as AlEtCl₂.

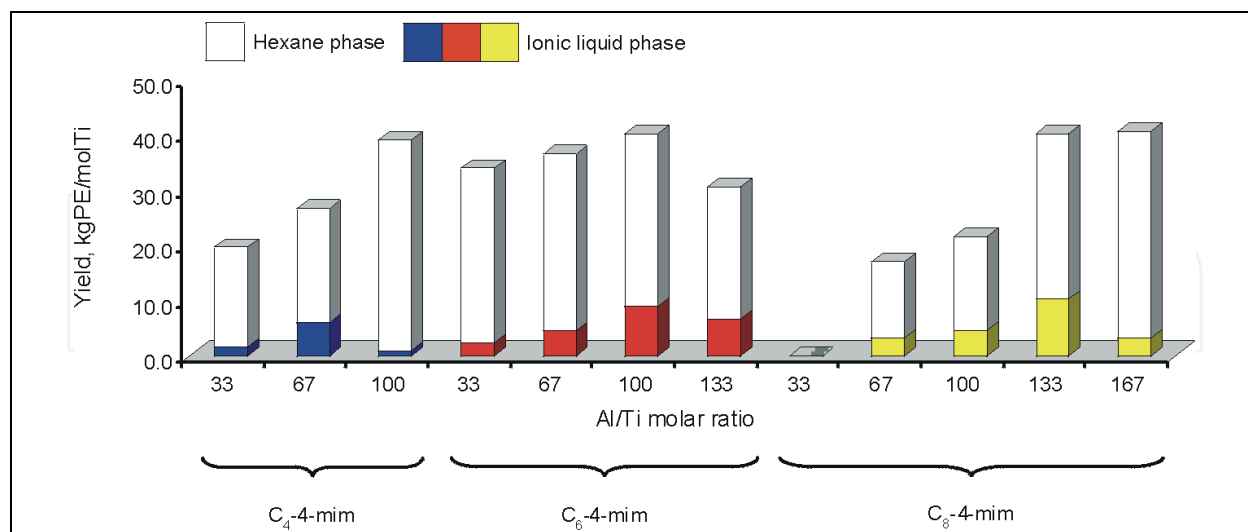


Fig. 6. The influence of the alkyl chain at the cation of the ionic liquids and the concentration of the AlEt₂Cl alkylaluminium activator on the performance of the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquid - [C_n-mim][AlCl₄] (n = 4,6,8), catalyst - Cp₂TiCl₂, activator - AlEt₂Cl, pressure - 0.5MPa, room temperature, reaction time - 60 min.

2.4 Pyridinium ionic liquids

Similar studies were carried out for the pyridinium ionic liquids. The pyridinium cation not only differs in its structure in comparison to the imidazolium cation, but also the position of the alkyl chain can be changed. 1-*n*-Alkyl-4-methylpyridinium chloroaluminates $[C_n\text{-4-mpy}][AlCl_4]$ were investigated at similar polymerisation conditions as for the imidazolium ionic liquids (Figure 7). It was found that the yield increases with the increase of the alkylaluminium concentration. Nevertheless at higher activator/catalyst molar ratios, the majority of the product remains in the ionic liquids, which is a disadvantageous phenomenon. Only at a lower activator/catalyst molar ratio ($Al/Ti = 67$) is the majority of the polymer product gathered in the hexane phase. In contrast to the imidazolium ionic liquids, the best results were obtained for the pyridinium cations with shorter alkyl chains ($[C_4\text{-4-mpy}][AlCl_4]$). This can particularly be seen at lower Al/Ti molar ratios.

The change of the position of the alkyl chain at the pyridinium cation was investigated on the $[C_8\text{-4-mpy}][AlCl_4]$ and $[C_8\text{-3-mpy}][AlCl_4]$ ionic liquids. In both cases the polymerisation yield and the transfer of the polymer to the hexane phase is slightly better for the ionic liquid having the alkyl chain at the *para* position at the pyridinium cation. This indicates that the position of the alkyl chain at the ionic liquid cation influences the performance of the biphasic process, although the effect is moderate. Generally, the application of pyridinium ionic liquids to the biphasic polymerisation results in higher yields in comparison to imidazolium analogues at similar reaction conditions.

To improve the performance of the biphasic polymerisation, the reaction time was extended twice (up to 120 min.). Advantageous increases in the amount of the product in the hexane phase as well as in the total polymerisation yield were observed. Again, the best result was obtained for the $[C_4\text{-4-mpy}][AlCl_4]$ ionic liquid with the shortest alkyl chain.

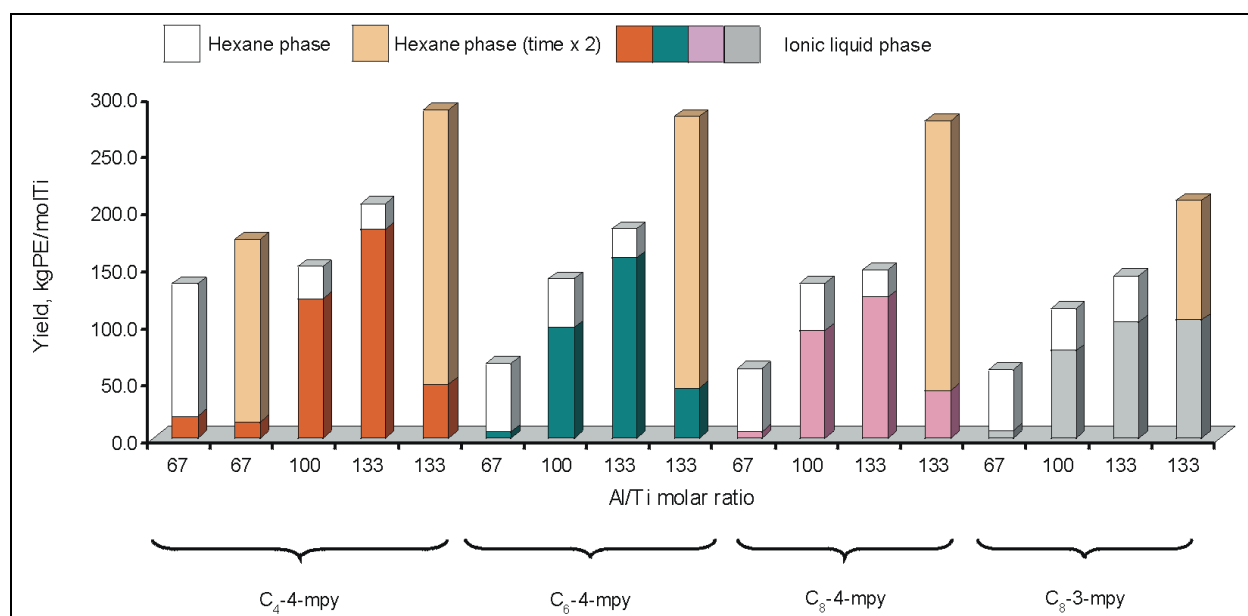


Fig. 7. The influence of the alkyl chain at the pyridinium cation and the concentration of the $AlEtCl_2$ alkylaluminium activator on the performance of the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquids: $[C_n\text{-4-mpy}][AlCl_4]$ ($n = 4,6,8$); $[C_8\text{-3-mpy}][AlCl_4]$, catalyst - Cp_2TiCl_2 , activator - $AlEtCl_2$, pressure - 0.5MPa, room temperature, reaction time - 60 min.

By contrast, the length of the alkyl chain at the pyridinium cations in comparison to imidazolium analogues has a negative effect, which can clearly be seen using the AlEt_2Cl activator instead of AlEtCl_2 (Figure 8). Similarly to the imidazolium ionic liquids, the application of the AlEt_2Cl activator results in a considerable decrease of the reaction yield. However, it should be noted that almost the entire amount of the polymer product is gathered in the hexane phase. This phenomenon is of great importance because it results in a product of high purity. Furthermore, the negligible amount of the product in the ionic liquid phase makes it possible to apply this phase in consecutive multi-step reactions. Thus, the recycling of both the catalyst and the ionic liquid can easily be done. It seems that the AlEt_2Cl activator could be successfully applied in a continuous flow process, whereas the AlEtCl_2 activator is better in a single reaction step.

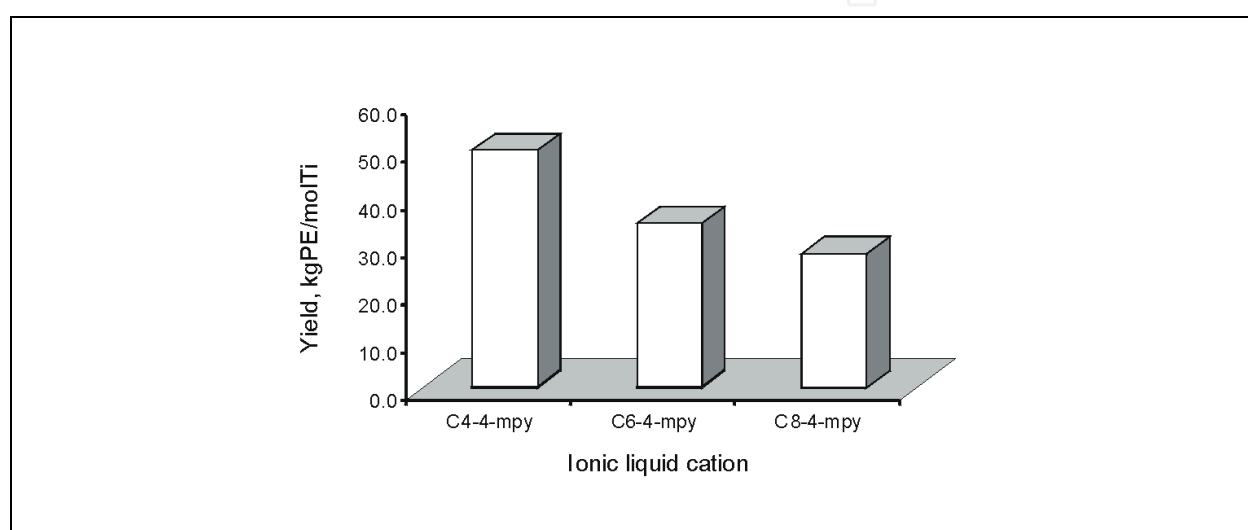


Fig. 8. The influence of the alkyl chain at the pyridinium cation and the concentration of the AlEt_2Cl alkylaluminium activator on the performance of the biphasic ethylene polymerisation. Polymerisation conditions: ionic liquid - $[\text{C}_n\text{-4-mpy}][\text{AlCl}_4]$ ($n = 4,6,8$), catalyst - Cp_2TiCl_2 , activator - AlEt_2Cl , $\text{Al/Ti} = 133$, standard pressure - 0.5MPa, room temperature, reaction time - 60 min.

2.5 Ionic liquids properties

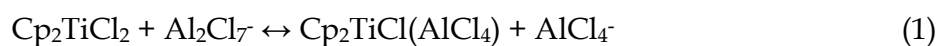
The presented results show that the structure of the ionic liquid cation has a considerable influence on the performance of the biphasic polymerisation. The structure of the cation influences the physical properties of the ionic liquids, such as density and viscosity (Olivier-Bourbigou, 2010).

Generally, an increase in the alkyl chain length leads to a decrease in the density and an increase in the viscosity of the ionic liquid. In biphasic ethylene polymerization the viscosity and the density of the ionic liquid play a key role in the dispersion of both phases, which influences the mass transfer of the product from the ionic liquid phase to the hexane phase. This can be seen the most clearly in the case of the polymerisations carried out in the imidazolium ionic liquids (Figure 5). In the case of the pyridinium analogues, the mass transfer seems to be more hindered, and this effect is much smaller.

For polymerisation performed at lower alkylaluminium (activator) concentration, the majority of the product is gathered in the hexane phase. This can be explained by the

presence of a relatively small number of active sites. In consequence, a smaller amount of the polymer is produced, but this does not exceed the amount of product which the system is able to transfer from the ionic liquid phase where the product is created to the hexane phase where the product is gathered. For the polymerisation performed at a higher alkylaluminium concentration, a greater number of active sites appears, which results in a greater amount of the polymer produced than the system is able to transfer to the hexane phase. Thus, a considerable amount of the product remains in the ionic liquid phase. This phenomenon is observed for all the ionic liquids studied. The polymerisation performed using the AlEt_2Cl compound support this conclusion. AlEt_2Cl is an activator of lower efficiency than AlEtCl_2 . It creates a smaller number of active sites, and thus, a smaller mass of the polymer product, but this is easily transferred to the hexane phase.

The optimum activator/catalyst molar ratio observed in the case of the polymerisation carried out in the imidazolium ionic liquids is another interesting phenomenon. Too low or too high a concentration of the alkylaluminium compound is disadvantageous and leads to a decrease of the reaction yield. This phenomenon is connected with the acidity of the ionic liquid phase. Carlin and Wilkes proved that only ionic liquids of the Lewis acid character are useful for the ethylene polymerisation reaction. The acid character of the chloroaluminate ionic liquid can be obtained by adding the correct amount of AlCl_3 . Usually, during the synthesis of the ionic liquids from AlCl_3 and the given chloride of the organic cation, an excess of AlCl_3 is added ($\text{AlCl}_3/[\text{C}_n\text{-mim}]\text{Cl} > 1$). However, at a higher concentration of the AlCl_4^- and Al_2Cl_7^- anions, complexation of the titanocene catalyst to either the $\text{Cp}_2\text{Ti}(\text{AlCl}_4)_2$ or $\text{Cp}_2\text{TiCl}(\text{Al}_2\text{Cl}_7)$ forms can occur (Carlin, Wilkes, 1990).



The proper acidity of the ionic liquid can be obtained using alkylaluminium compounds containing chlorine atoms. These compounds, such as the AlEtCl_2 applied in this work, lead to the creation of various anions in the reaction medium: AlCl_4^- , Al_2Cl_7^- , $\text{Al}_2\text{EtCl}_6^-$, AlEtCl_3^- , $\text{Al}_2\text{Et}_2\text{Cl}_5^-$. The optimum parameters of the chloroaluminate ionic liquid applied as a medium of the catalyst for the polymerisation depends on the amount and kinds of the anions. Higher concentrations of the AlCl_4^- and AlEtCl_3^- anions, of neutral character, considerably decrease the acidity of the chloroaluminate ionic liquid. In contrast, higher concentrations of the Al_2Cl_7^- and $\text{Al}_2\text{EtCl}_6^-$ anions result in the ionic liquid being too acidic, which also leads to a decrease of the polymerisation yield. Therefore, the judicious selection of the kind and amount of the alkylaluminium Lewis acid is very important when tailoring the acidity of the ionic liquid. The presented results indicate that the application of the AlEtCl_2 compound, which reveals a higher Lewis acidity in comparison to AlEt_2Cl , results in a better performance of the ionic liquid in the polymerisation reaction (Chauvin, 1990; Thiele, de Souza, 2007).

The optimum activator/catalyst molar ratio not only enables the reduction of the titanium compound, but also creates the appropriate environment for the polymerisation reaction, which results from the correct proportion of the chloroaluminate anions being present in the ionic liquid medium.

It is known that in the homogeneous metallocene systems, the active site is represented by the cationic form of the metallocene; Cp_2MR^+ . Thus, the necessary condition for the polymerisation reaction is:

- i. detachment of the AlCl_4^- group and creation of the unsaturated Cp_2TiR^+ , according to the equation:



- ii. exchange of the AlCl_4^- group by ethylene molecule and creation of the $\text{Cp}_2\text{TiR}(\text{CH}_2\text{CH}_2)^+$ complex:



In both cases, the centre of the polymerisation reaction is the cationic complex, created by the break of the M-Cl bond, which is stronger for Zr and Hf and weaker for Ti. Therefore, the inactivity of the Zr and Hf compounds results from the stronger M-Cl bonds, which make it impossible to create the active cationic form $[\text{Cp}_2\text{MR}^+]$ (Carlin, Wilkes, 1990). It should be noted, however, that the chloroaluminate ionic liquid participates in the creation of the active centre, which is supported by literature (Chauvin, 1997; Simon, 1998; Bernardo-Gusmao, 2003).

3. Polyethylene properties

The presented biphasic polymerisation experiments show that the polyethylene product is present in both the ionic liquid and hexane phases. According to the concept of biphasic polymerisation, the product gathered in the hexane phase is the most important. Therefore only the properties of this polyethylene have been analysed. The polyethylene from the ionic liquid phase is contaminated by the products of decomposition of the catalyst, activator, and ionic liquids, which means that it is impossible to determine the PE properties correctly.

The data presented in Table 1 show the influence of the imidazolium ionic liquids on the properties of the PE produced. The obtained polyethylene was linear in character. On average, 3.0-9.4 methyl groups on the 1000 methylene groups occur. The melting temperature ($\sim 133^\circ\text{C}$) is relatively narrow and typical for commercial HDPE (Vasilie, Pascu, 2005). The high crystallinity degree ($\sim 86\%$) should be noted. This value varies depending on the length of the alkyl chain at the ionic liquid cation; the lowest is for $[\text{C}_4\text{-mim}][\text{AlCl}_4]$ ($\sim 82\%$), and the highest for $[\text{C}_8\text{-mim}][\text{AlCl}_4]$ ($\sim 87\%$). Another advantageous feature of the polyethylene product is a high value of the bulk density, which again varies depending on the ionic liquid applied. Again, the lowest value was obtained for $[\text{C}_4\text{-mim}][\text{AlCl}_4]$ ($\sim 230 \text{ g/dm}^3$) and the highest for $[\text{C}_8\text{-mim}][\text{AlCl}_4]$ ($\sim 470 \text{ g/dm}^3$). Such high values of the PE bulk density can be obtained only for the heterogeneous metallocene catalyst (Kang, 1999; Razavi, 2000; Jang, 2003; Wei, 2004; Ochędzan-Siodłak, 2005; Hammawa, 2006). In the case of the homogeneous systems, the bulk density usually does not exceed 100 g/dm^3 (Soares, 2000; Lee, 2000). The high values of the crystallinity degree and bulk density of the polyethylene obtained show a high level of the molecular order and indicate good mechanical parameters of the polymer product. Nevertheless, the polyethylene obtained has a relatively small molecular weight (M_w) in the range of 70 000–170 000 g/mol. The molecular weight decreases with the increase of the activator/catalyst molar ratio. Therefore, an increase of the activator concentration results in shorter PE chains. It indicates

that the alkylaluminium compound participates, most probably, in the chain termination reaction. The molecular weight distribution is monomodal (MWD from 4.3 to 7.2). This is characteristic for the polymer obtained using supported metallocene catalysts. The polyethylene obtained using the AlEt_2Cl activator has a similar melting temperature, crystallinity degree, molecular weight, molecular weight distribution, and linearity to the analogue polymer obtained using the AlEtCl_2 activator, regardless of the ionic liquid used. However, the bulk density is lower when AlEt_2Cl is applied.

| Item | Activator/Catalyst molar ratio | T_m (°C) | Crystallinity (DSC) (%) | $M_w \times 10^{-3}$ (g/mol) | MWD | Bulk density (g/dm ³) | $\text{CH}_3/1000\text{CH}_2$ |
|---|--------------------------------|------------|-------------------------|------------------------------|-----|-----------------------------------|-------------------------------|
| [C₄mim]⁺[AlCl₄]⁻ | | | | | | | |
| 1 | 67 | 134 | 86.8 | 159.6 | 4.4 | 243 | 3.7 |
| 2 | 100 | 133 | 83.5 | 86.7 | 5.8 | 220 | 6.3 |
| 3 | 133 | 137 | 81.6 | 71.7 | 4.3 | 240 | 3.0 |
| [C₆mim]⁺[AlCl₄]⁻ | | | | | | | |
| 4 | 67 | 133 | 85.9 | 121.5 | 6.2 | - | 7.6 |
| 5 | 100 | 132 | 86.4 | 110.0 | 6.8 | 370 | 7.3 |
| 6 | 133 | 132 | 86.6 | 45.9 | 4.8 | 440 | 7.0 |
| 7 ^a | 100 | 133 | 85.5 | 116.3 | 4.3 | 170 | 9.4 |
| [C₈mim]⁺[AlCl₄]⁻ | | | | | | | |
| 8 | 67 | 135 | 89.2 | 165.6 | 7.2 | - | - |
| 9 | 100 | 134 | 88.6 | 129.2 | 6.8 | 340 | 6.2 |
| 10 | 133 | 133 | 85.8 | 82.5 | 5.3 | 470 | 8.3 |
| 11 ^a | 100 | 134 | 80.5 | 77.8 | 5.4 | 160 | 7.0 |
| ^a AlEt_2Cl activator | | | | | | | |

Table 1. Selected properties of the polyethylene produced using imidazolium ionic liquids in the biphasic polymerisation

The application of the pyridinium ionic liquid in the biphasic polymerisation results in a polyethylene product with slightly different properties than that obtained using the imidazolium ionic liquids (Table 2). It is a linear polyethylene and the number of branches (from 4.3 to 12.9 of the CH_3 groups per 1000 CH_2 groups) is comparable for all the samples analysed. The number of branches increases with an increase in the activator concentration, regardless of the ionic liquid used. The melting temperatures (127-130°C) are lower but the molecular weights ($M_w = 100\,000\text{--}270\,000$ g/mol) are higher than for the PE samples obtained in the biphasic polymerisation using imidazolium ionic liquids. It should be noted that the lowest M_w have PE samples obtained using $[\text{C}_8\text{-3-mpy}][\text{AlCl}_4]$. The molecular weight distributions (MWDs) of the studied samples are relatively broad, from 3.1 to 6.9. Again, the distinguishing feature of the PE produced is the high bulk density, which reaches up to a value of 520 g/dm³, which corresponds to that of the polyethylenes obtained over supported metallocene catalysts. A decrease of the bulk density is observed with the increase of the activator/catalyst molar ratio. The position of the alkyl chain at the pyridinium cation has an influence on the bulk density. The polyethylene produced using the $[\text{C}_8\text{-4-mpy}][\text{AlCl}_4]$ ionic liquid has a higher bulk density than that obtained using $[\text{C}_8\text{-3-mpy}][\text{AlCl}_4]$ (Al/Ti=67 and 100).

All the studied PE samples reveal an exceptionally high crystallinity degree, with an average value of 93%, as determined by the DSC method. Such a high crystallinity is atypical for PE obtained using a metallocene catalyst (Prasad, 1999; Wei, 2004) and it corresponds to that of the commercial HDPE (crystallinity = 77-90%) obtained using Ziegler-Natta catalysts (Doak, 1986).

The polyethylene samples obtained using the AlEt_2Cl activator revealed considerable purity due to the efficient mass transfer to the hexane phase of the polymer produced. They reveal much lower molecular weights, bulk densities, and crystallinity - similar to those of the polyethylene obtained in the biphasic process using imidazolium ionic liquids (Ochędzan-Siodłak, 2008). Generally, the polyethylene obtained using AlEtCl_2 as the activator is characterised by better properties than that obtained using AlEt_2Cl .

| Item | Activator/Catalyst molar ratio | T_m (°C) | Crystallinity (DSC) (%) | $M_w \times 10^{-3}$ (g/mol) | MWD | Bulk density (g/dm ³) | $\text{CH}_3/1000\text{CH}_2$ |
|---|--------------------------------|------------|-------------------------|------------------------------|-----|-----------------------------------|-------------------------------|
| [C ₄ -4-mpy][AlCl ₄] | | | | | | | |
| 1 | 67 | 128 | 94.0 | 261.6 | 5.9 | 370 | 5.9 |
| 2 | 100 | 126 | 95.0 | 233.0 | 6.7 | 215 | 8.9 |
| 3 | 133 | 127 | 95.1 | 151.5 | 5.4 | - | 9.9 |
| 4 ^a | 133 | 129 | 94.2 | 142.9 | 6.7 | 165 | 9.1 |
| [C ₆ -4-mpy][AlCl ₄] | | | | | | | |
| 5 | 67 | 129 | 94.9 | 260.0 | 5.5 | 444 | 5.2 |
| 6 | 100 | 128 | 93.1 | 229.3 | 6.7 | 283 | 7.1 |
| 7 | 133 | 126 | 95.1 | 150.9 | 6.1 | 136 | 12.9 |
| 8 ^a | 133 | 127 | 90.6 | 130.1 | 6.9 | 145 | 11.1 |
| [C ₈ -4-mpy][AlCl ₄] | | | | | | | |
| 9 | 67 | 129 | 96.0 | 266.8 | 6.9 | 520 | 4.4 |
| 10 | 100 | 128 | 95.0 | 222.9 | 5.4 | 395 | 5.3 |
| 11 | 133 | 133 | 93.0 | 158.6 | 5.9 | 210 | 6.2 |
| 12 ^a | 133 | 130 | 87.4 | 122.5 | 5.6 | 137 | 9.8 |
| [C ₈ -3-mpy][AlCl ₄] | | | | | | | |
| 13 | 67 | 128 | 96.0 | 141.3 | 3.4 | 481 | 5.0 |
| 14 | 100 | 128 | 98.0 | 138.2 | 3.9 | 357 | 6.0 |
| 15 | 133 | 127 | 98.0 | 111.5 | 3.1 | - | 8.1 |

^a AlEt_2Cl activator

Table 2. Selected properties of the polyethylene produced using pyridinium ionic liquids in the biphasic polymerisation

The presented results show that the polyethylene product obtained in the biphasic process joins the properties of the polyethylenes obtained using the homogenous and heterogeneous metallocene catalysts (a low molecular weight as well as broad molecular weight distribution and high bulk density, respectively). Moreover, the product is characterised by a high crystallinity degree resulting from the high level of the macromolecular order, which is particularly observed for the samples obtained from the pyridinium ionic liquids. Properties such as molecular weight, bulk density, and crystallinity degree can be modified by both the kind of the alkyl chain at the ionic liquid cation and the concentration of the alkylaluminium compound.

4. Conclusion

The presented studies describe the biphasic ionic liquid/hexane polymerisation of ethylene using a titanocene catalyst. For the ionic liquids, imidazolium and pyridinium chloroaluminates were applied. It was found that the catalyst is stable in the polymerisation reaction and firmly immobilized in the ionic liquid. Therefore, application of ionic liquids as media of the catalyst seems to be an interesting alternative to the catalyst's heterogenisation on the solid carrier. The studied biphasic mode makes it possible to re-use (recycle) both the catalyst and the ionic liquid phase. The traditional alkylaluminium compounds are more suitable activators for the titanocene catalyst than methylaluminoxane, which is considered as the most effective activator for metallocene catalysts. Polyethylene (PE) formed in the ionic liquid phase is progressively transferred to the hexane phase. Thus, the polymer is characterized by a high purity and can easily be separated from the reaction mixture by a simple decantation technique.

It is possible to influence the performance of the biphasic polymerisation and the properties of the polymer product by changing the character of the ionic liquid. This can be done by the modification of the cationic and anionic parts of the ionic liquid. In the presented work the 1-*n*-alkyl-3-methylimidazolium and 1-*n*-alkyl-4-methylpyridinium cations with alkyl chains of various length were investigated. The chloroaluminate anions can be modified by the choice of the kind and the concentration of the alkylaluminium compound, which is also applied as the catalyst activator. The following alkylaluminium compounds were investigated: AlEt₃, AlEt₂Cl, AlEtCl₂, and MAO. The results obtained using compounds containing the chlorine atom, AlEtCl₂ and AlEt₂Cl were better than when methylaluminoxane was applied. The AlEtCl₂ compound turned out to be the most suitable for the biphasic ethylene polymerisation as regardless of the ionic liquid cation used, the highest yields were obtained. It should be noted that the reaction yield depends on the concentration of the alkylaluminium compound. This can be explained by the balance of the various chloroaluminate anions created, which influence the acidity of the ionic liquids, which is necessary for the polymerisation reaction. The concentration of the alkylaluminium compound, described in the form of activator/catalyst molar ratio (Al/Ti), determines the amount of the polymer product gathered in the hexane phase. Generally, the lower the Al/Ti molar ratio, the greater amount of product present in the hexane phase and a correspondingly smaller amount remaining in the ionic liquid phase. Relatively low activator/catalyst molar ratios result in a low concentration of the active sites, and the amount of the polymer produced does not exceed the ability of the biphasic system to transfer the product from the ionic liquid to the hexane phase. Therefore, for each ionic liquid an optimum concentration of the alkylaluminium compound can be determined. For the imidazolium ionic liquids, the longer the alkyl chain at the cation the better the mass transfer of the product to the hexane phase. The length of the alkyl chain at the imidazolium cation changes the physical properties of the ionic liquids, particularly density and viscosity, which influence the dispersion and separation of both phases. For the pyridinium ionic liquids such a tendency is not observed. The transfer of the product to the hexane phase is best with a shorter alkyl chain at the pyridinium cation and only at a lower concentration of the alkylaluminium compound. Although the application of pyridinium ionic liquids results in better total yield (from both the ionic liquid and hexane phases), the mass transfer of the product to the hexane phase is hindered at higher AlEtCl₂ concentrations. This can be overcome, however, by extending the reaction time.

The analysis of the physical and molecular properties of the polyethylene product obtained in the biphasic process shows that regardless of the ionic liquid used, the product displays unique properties, particularly a non-typical, very high crystallinity degree - up to 95%. It is also possible to control the selected properties of the polymer product, e.g. the melting point, crystallinity degree and bulk density (Ochędzan-Siodłak et al., 2007; 2008; 2009; 2010). The presented results indicate that the biphasic polymerisation using ionic liquid as a medium of the catalyst is an interesting option, and even desirable from the point of view of modern green chemistry. It also makes it possible to obtain a polymer product with interesting properties, which can be tailored by the change of the ionic liquid's parameters. Further investigation should be focused on the elimination of the disadvantageous features of the biphasic polymerisation. It is particularly important to improve the catalytic performance of the system, the mass transfer of the product, and the control of the polymer morphology. A promising way to fulfil these requirements could be application of the supported ionic liquid phase (SILP) methodology, where the ionic liquid containing an organometallic catalyst is anchored on a solid carrier (Valkenberg et al., 2001; 2002; Mehnert, 2005; Riisager et al., 2006). This method makes it possible to control, simultaneously, the course of the polymerisation reaction and the physical and chemical properties of the polymer product. Additionally, the amount of the ionic liquid phase can be considerably reduced and the performance of the catalyst can be improved, while the catalyst re-use and the easy separation procedure can be maintained (Gu, Li, 2009).

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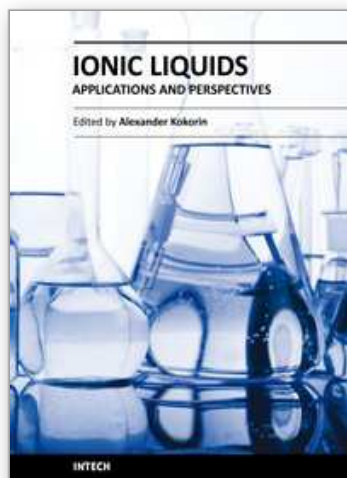
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