Annex 3

SELF-PRESENTATION

1. Name Family Name

Wioletta Ochędzan-Siodłak

2. Scientific degrees

1996	Master of Science Faculty of Mathematics, Physics and Chemistry, University of Opole, Opole.
2004	Doctor of chemical science, Faculty of Mathematics, Physics and Chemistry, University of Opole, Opole Ph. D. dissertation entitled: *Metallocene catalysts immobilized on magnesium complex carrier for ethylene polymerization* Promotor: prof. dr hab. inż. Maria Nowakowska

3. Information about previous and current employment

1996 – 2004	Assistant, Institute of Chemistry, Faculty of Mathematics, Physics and Chemistry, University of Opole
2004 – 2008	Adjunct, Institute of Chemistry, Faculty of Mathematics, Physics and Chemistry, University of Opole
2008 – presently	Adjunct, Faculty of Chemistry, University of Opole

4. Scientific achievement, according with article 16 paragraph 2 of the act edited 14 March 2003 about Academic Degree and Academic Title as well as Degrees and Title in Art (Dz. U. No 65, item 595 with changes)

Scientific achievement is a series of thematic publications composed of: 12 publications indexed in the JCR database and chapter in English monograph, covering one review (H1) and own research (H2-H14).

A) Title of scientific achievement:

METALLOCENE AND POSTMETALLOCENE CATALYST SYSTEMS WITH IONIC LIQUID FOR ETHYLENE POLYMERIZATION

B) List of publications included in the scientific achievement arranged according to the order of discussion

No **authors, title, volume, year, pages, impact factor from the year of release, estimate of own contribution**

H1 W. Ochędzan-Siodłak: Ciecze jonowe w oligomeryzacji i polimeryzacji olefin (Ionic liquids in olefins oligomerization and polymerization , *Wiad. Chem.* 63 (2009) 9-10, 277-281. (IF_{2009}=0)
Review work was done on its own. Own contribution 100%.

H2 W. Ochędzan-Siodłak*, B. Sacher-Majewska: Biphasic ethylene polymerisation using ionic liquid over a titanocene catalyst activated by an alkyl aluminium compound, *Eur. Polym. J.* 43 (2007) 3688-3694. (IF_{2007}=2,248)
I planned the work. I performed ethylene polymerization in a biphasic system. I participated in the study of properties of obtained polymers. I interpreted results. I edited the publication. I made the correction work after review. I rate my percentage contribution as 90%.

H3 W. Ochędzan-Siodłak*, P. Pawelska: Chloroaluminate ionic liquids as a medium of titanocene catalyst activated by alkyl aluminium compounds for ethylene polymerization, *Polimery* 53 (2008) 371-376. (IF_{2008}=0)
I planned the work. I have co-operated in ethylene polymerization in biphasic systems led by Paulina Pawelska (Adamek) within the framework of her master's thesis that I supervised. I conducted an analysis of the properties of the obtained polymers. I have interpreted the results. I have edited the publication. I made the correction of manuscript after review. My contribution is 80%.

H4 W. Ochędzan-Siodłak*, K. Dziubek, D. Siodłak: Biphasic ethylene polymerization using 1-*n*-alkyl-3-methylimidazolium tetrachloroaluminate ionic liquid as a medium of the Cp_2TiCl_2 titanocene catalyst, *Eur. Polym. J.* 44 (2008) 3608-3614. (IF_{2008}=2,143)
I planned the work. I co-operated in the synthesis of ionic liquids with dr Dawid Siodłak. I co-operated in ethylene polymerization in biphasic system led by Katarzyna Dziubek within the framework of her master's thesis that I supervised. I interpreted the results. I edited the publication. I made the correction of manuscript after review. My contribution is 70%.

H5 W. Ochędzan-Siodłak*, K. Dziubek, K. Czaja: Effect of immobilization of titanocene catalyst in aralkyl imidazolium chloroaluminate media on performance of biphasic ethylene polymerization and polyethylene properties, *Polym. Bull.* 70 (2013) 1-21. (IF_{2013}=1,491)
I planned the work. I co-operated in ethylene polymerization in biphasic system led by Katarzyna Dziubek within the framework of Ph. D. thesis that I supervised, as well as in analysis of the properties of obtained polymer. I interpreted the results. I edited the publication. I made the correction of manuscript after review. My contribution is 70%.

H6 W. Ochędzan-Siodłak*, K. Dziubek: Improvement of biphasic polymerization by application of binary ionic liquid mixture, *Chem. Eng. Proc.* 72 (2013) 74-81. (IF_{2013}=1,959)

I planned the work. I co-operated in the synthesis of ionic liquids and ethylene polymerization in biphasic system led by Katarzyna Dziubek within the framework of Ph. D. thesis that I supervised, as well as in analysis of the properties of obtained polymer. I interpreted the results. I edited the publication. I made the correction of manuscript after review. My contribution is 70%.

H7 W. Ochędzan-Siodłak*, K. Dziubek, K. Czaja: Comparison of imidazolium and pirydinium ionic liquids as mediums of the titanocene catalyst for biphasic ethylene polymerisation, *Polimery* 54 (2009) 501-506. (IF_{2009}=0)

I planned the work. I co-operated in the synthesis of ionic liquids and ethylene polymerization led by Ph. D. student Katarzyna Dziubek within the framework of her thesis that I supervised, as well as in analysis of the properties of obtained polymer. I interpreted the results. I edited the publication. I made the correction of manuscript after review. My contribution is 70%.

H8 W. Ochędzan-Siodłak*: Ionic liquids in biphasic ethylene polymerization [in] Ionic Liquids: Applications and Perspectives. Aleksandar Kokorin (ed.). Publisher: InTech Web. Org., Croatia 2011, pp. 29-44. ISBN: 978-953-307-248-7.

Chapter in English monograph. Review work was done on its own. Own contribution 100%.

H9 W. Ochędzan-Siodłak*, K. Dziubek, K. Czaja, S. Rabiej, R. Szatanik: High crystallinity polyethylene obtained in biphasic polymerization using pyridinium chloroaluminate ionic liquid, *J. Polym. Res.* 21 (2014) 558-566. (IF_{2014}=1,920)

I planned the work. I co-operated with Ph. D. student Katarzyna Dziubek that I supervised in the synthesis of ionic liquids and determination of properties of polyethylene. I interpreted the results. Edition of the publication was in majority my work. I made the correction of manuscript after review. My contribution is 50%.

H10 W. Ochędzan-Siodłak*, K. Dziubek, D. Siodłak: Densities and viscosities of imidazolium and pyridinium chloroaluminate ionic liquids, *J. Mol. Liq.* 177 (2013) 85-93. (IF_{2013}=2,083)

I planned the work. I co-operated with Ph. D. student Katarzyna Dziubek in the synthesis and determination of density and viscosity of ionic liquids that I supervised. I interpreted the results. Edition of the publication was in majority my work. I made the correction of manuscript after review. My contribution is 60%.

H11 W. Ochędzan-Siodłak*, K. Dziubek: Metallocenes and post-metallocenes immobilized on ionic liquid-modified silica as catalysts for polymerization of ethylene, *Appl. Catal. A Gen.* 484 (2014) 134-141. (IF_{2014}=3,942)

I planned the work. I co-operated with Ph. D. student Katarzyna Dziubek in the synthesis of metallocene and post-metallocene catalyst systems as well as in ethylene polymerization that I supervised. I interpreted the results. The edition of publication and the correction of manuscript after review were in majority my work. My contribution is 70%.

H12 W. Ochędzan-Siodłak*, A. Bihun: Direct synthesis of fibrous high molecular weight polyethylene using vanadium catalysts supported on SiO_2-ionic liquid system, *Polym. Int.* 64 (2015) 1600-1606. (IF_{2015}=2,414)

I planned the work. I co-operated with M. S. student Anna Bihun that I supervised in the synthesis of catalyst systems, ethylene polymerization, and analysis *of the properties of obtained polymers. I interpreted the results. I edited the publication. I made the correction of manuscript after review. My contribution is 80%.*

H13 W. Ochędzan-Siodłak*, A. Bihun, A. Olszowy, M. Rajfur, T. Jesionowski, K. Siwińska-Stefańska: Ethylene polymerization using vanadium catalyst supported on silica modified by pyridinium ionic liquid, *Polym. Int.* 65 (2016) 1089-1097. (IF_{2015}=2,07)

I planned the work. I supervised and co-operated with Ph.D. student Anna Bihun in the synthesis of catalyst systems as well as with M.S. student Aleksandra Olszowy, as promoter, in the ethylene polymerization, and the analysis of properties of obtained polymers. I interpreted the results. I edited the publication. I made the correction of manuscript after review. My contribution is 60%.

H14 W. Ochędzan-Siodłak*, A. Bihun: Copolymerization of ethylene with norbornene or 1-octene using supported ionic liquid systems, *Polym. Bull.* 74 (2017) 2799-2817. (IF_{2015}=1,430)

I planned the work. As auxiliary promoter, I supervised and co-operated with Ph.D. student Anna Bihun in the synthesis of catalyst systems and ethylene (co)polymerization with norbornene and 1-octene as well as in analysis of the properties of obtained (co)polymers. I interpreted the results. I edited the publication. I made a correction of the manuscript after review. My contribution is 70%.

* corresponding author

Statements of all co-authors, defining individual contribution to the above publications can be found in Annex 4.

Patents related to the subject of scientific achievement:

HD1 PL 218014 W. Ochędzan-Siodłak, K. Dziubek, K. Czaja: Sposób otrzymywania polietylenu w środowisku z cieczą jonową (Method of obtaining polyethylene in an ionic liquid medium). Patent application No P.395396 of 22 June 2011. Date of publication 30 September 2014.

HD2 PL 218644 W. Ochędzan-Siodłak, K. Dziubek, K. Czaja: Sposób wytwarzania polietylenu (Production method of polyethylene). Patent application No P. 402237 of 24 December 2012. Date of publication 30 January 2015.

HD3 PL 225211 W. Ochędzan-Siodłak, K. Dziubek, K. Czaja, A. Bihun: Sposób wytwarzania włókien polietylenowych (Production method of polyethylene fibers). Patent application No P.409860 of 20 October 2014. Date of publication 8 September 2016.

C) **Discussion of the scientific aforementioned achievement and the results obtained, together with a discussion of their possible application**

INTRODUCTION

Polyethylene (PE) is the most important representative of polyolefins - the largest group of industrially produced plastics. The PE has gained popularity mainly due to easy processing, low production costs, chemical neutrality, and environmental performance [1, 2]. Nowadays, the enormous demand for environmentally friendly polymeric materials as well as polymers having specific and valuable properties contributes to the continuous search for more active and selective organometallic catalysts for olefin polymerization. In this field, metallocene and post-metallocene catalysts deserve special attention due to the tremendous possibilities of differentiating their structure, which allow planning and controlling both the course of polymerization and properties of the polymers obtained in a wide range [3-5].

Homogeneous metallocene systems, and to a less extent also post-metallocene, reveal very high activity in ethylene polymerization and high homogeneity of the active centers, so that the reaction proceeds in a much more selective way than with classical heterogeneous systems based on transition metal halides. However, this type of catalysts requires the use of aromatic solvents and a large excess of expensive activator - methylaluminoxane (MAO). From the technological point of view, there are the following disadvantages: contamination of the reactor by polymer products of low molecular weight (reactor fouling), lack of catalyst reuse, and lack of control of polymer morphology. The use of homogeneous systems dissolved in reaction medium causes difficulties with the separation of final product, limiting the application in industrial processes, especially in fluidal systems [4-7].

The anchorage of metallocene and post-metallocene catalysts on a solid carrier, commonly silica or magnesium chloride, limits most of the drawbacks of homogeneous systems, among others, reduces the amount of activator and improves the morphological properties of polymers. However, this kind of heterogenization proved to be a multi-step and technically difficult process. For metallocene catalysts, it usually results in a significant reduction in activity, in comparison to their homogeneous analogues, and a change in the molecular characteristics of the resulting polymer. In addition, desorption of the transition metal compound from the surface of carrier and the deactivation of active sites during the polymerization are very common in such systems. Moreover, it is difficult to estimate the influence of support and the method of immobilization on the properties of catalyst [7-13].

It is therefore reasonable to search for alternative methods of synthesis of organometallic catalysts for ethylene polymerization, which could provide the advantages, and at the same time, eliminate the disadvantages of homogeneous and heterogeneous catalysts while giving the possibility of obtaining polymers with specific properties.

Biphasic liquid-liquid system is such unconventional method to immobilize catalysts. In this system, consisting of two immiscible solvents, the catalyst is in one phase while the substrates and products remain in another phase. The process enables mild conditions, good yield and selectivity, multiple reuse of the catalytic phase, and simple product separation [14-15]. In recent times, biphasic systems with ionic liquid as one of the phases have become particularly popular. Ionic liquids have been viewed as an alternative to conventional volatile organic solvents. This class of compound gains interest due to their structural diversity and physical and chemical properties that can be broadly tailored by the appropriate selection of ionic components [16-20]. The properties of ionic liquids affect their multidirectional application [16-26], including organic synthesis, where they have proven to be effective solvents, catalysts, activators and/or ligands. They are successfully used in Friedel-Crafts, Heck, Diels-Alder, esterification, hydrogenation, hydroformylation, and dimerization, oligomerization, and polymerization [23-26]. The significant advantages of biphasic systems with ionic liquid are; high efficiency, selectivity, easy separation of the high-purity products, and the ability to reuse the catalytic phase in subsequent reaction cycles.

Another concept of the application of ionic liquids in organic synthesis is the Supported Ionic Liquid (SIL) [27-29]. In this method a thin layer of ionic liquid with a catalyst is immobilized on a solid support of high porosity. In this way the catalyst maintains the features of homogeneous system, which ensures high efficiency and selectivity of reaction. Also, difficulties associated with supported catalyst systems are eliminated. Not only the problem of evaporation of liquid phase from the carrier is limited, the ionic liquids have low vapor pressures, but also the direct effect of the support on the catalyst. It is also worth emphasizing that the amount of ionic liquid is reduced in comparison to biphasic systems, the rate of reaction is increased, due to the shortening of substrate diffusion route. The difficulties of mass transfer between the phases are also excluded. Due to these advantages, the SIL systems have proven to be particularly effective, amongst other, in the hydroformylation, cycloaddition, Fischer esterification, trans-esterification and even Friedel-Crafts alkylation and acylation [25-32]. The concept of the supported ionic liquid, as an alternative to typical heterogenization, has been also used to synthesize organometallic catalysts for the oligomerization of olefins [33-35].

RESEARCH OBJECTIVE AND DISCUSSION OF RESULTS OF RESEARCH

A scarce literature data on the use of ionic liquids in olefin polymerization catalyzed by transition metal compounds prompted me to explore this research topic.

The aim of my research was evaluation the efficiency of selected metallocene and post-metallocene catalysts systems containing different types of ionic liquids in coordinative ethylene polymerization and the investigation of properties of obtained polymers.

The research was conducted within the framework of two research projects: 1) No. 3 T09B 003 29 (MNiSW) entitled " *Organometallic catalytic complexes with ionic liquids for ethylene polymerization*” and 2) No. N N209 335337 MNiSW/NCN entitled “*Bihpasic ethylene polymerazation using metallocene catalyst immobilized in ionic liquids*”, made in years 2005-2012.

Ethylene polymerization in biphasic system with ionic liquids

Based on the literature review on the use of ionic liquids in biphasic olefin oligomerization and polymerization catalyzed by transition metal complexes [**H1**], I found that the most effective in these processes are the ionic liquids consisted of imidazolium cation and chloroaluminate anions [36-40]. Particularly pioneering was the Chauvin study, where the 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate ionic liquid ($[C_4\text{-mim}][AlCl_4]$) was applied in the dimerization of propylene and *n*-butene, carried out in a biphasic system with nickel complexes. The effect of acidity of the ionic liquid on olefin oligomerization was noted, and this reaction was possible only in the presence of acidic chloroaluminate anions $Al_2Cl_7^-$, when molar ratio aluminium chloride to 1-*n*-butyl-3-methylimidazolium chloride ($AlCl_3$ / $[C_4\text{-mim}]Cl$) was > 1 [37]. Apart $AlCl_3$, alkylaluminum compounds such as $AlEtCl_2$ or $AlEt_2Cl$ can also be effective as regulators of acidity [37, 39]. They contribute to the formation in the reaction medium not only $AlCl_4^-$ or $Al_2Cl_7^-$ anions, but also of various types of chloroethylaluminate anions such as $AlEtCl_3^-$, $Al_2EtCl_6^-$, $Al_2Et_2Cl_5^-$ or $Al_3EtCl_9^-$, which increase reaction yields [40]. Similar conclusions regarding the polyreactions progress performed in the ionic liquid, were reported by Carlin, who applied the 1-ethyl-3-methylimidazolium tetrachloroaluminate ionic liquid ($[C_2\text{-mim}][AlCl_4]$) in the coordinative ethylene polymerization with $TiCl_4/AlEtCl_2$ catalytic system [38] or metallocenes Cp_2MtCl_2 (where Mt is Ti, Hf, Zr) activated by alkylaluminum compounds ($AlCl_{3-x}R_x$, where R=Me, Et) [36]. The traces of polyethylene were obtained using Ziegler-Natta catalyst, whereas in the case of metallocenes, the catalytic activity was shown only for titanocene, below 10 kg PE $(\text{mol Mt} \cdot h)^{-1}$. It was undoubtedly associated with the phenomenon of complexation of metallocene with chloride or chloraluminate ions. The polymerization reaction can only take place in acidic ionic liquids, where the $AlCl_4^-$ and $Al_2Cl_7^-$ ions are present, which allow for the formation of the $[Cp_2MtR^+]$ moiety, which is active in the polymerization. However, this proved to be possible only in the case of titanocene, where the catalytically active cationic complex $[Cp_2TiR^+]$ was formed by breaking up the Ti-Cl bond in bridging structure Ti-Cl-Al of the complex, much weaker in the case of Ti than Zr and Hf, what explains inactivity of these metallocenes [36].

The works of Chauvin as well as Carlin and Wilkes have become the starting point for my research on the use of ionic liquids in coordinative ethylene polymerization in a biphasic system (Figure 1, Table 1).

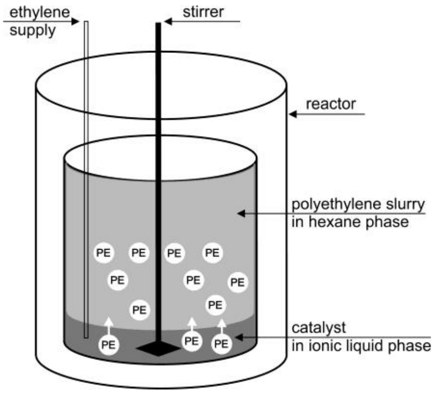
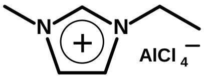
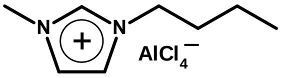
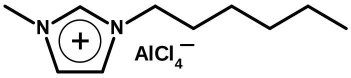
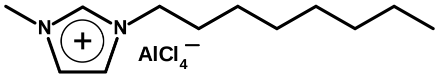
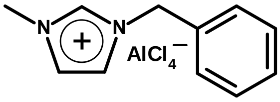
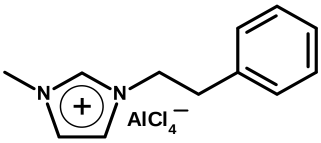
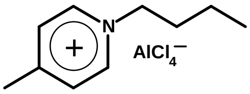
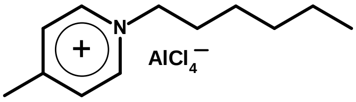
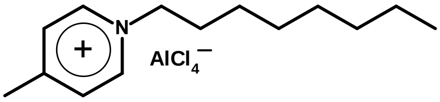
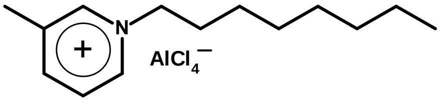
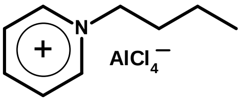
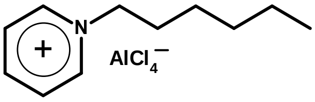
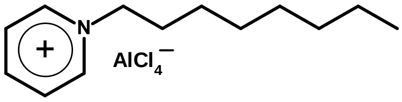


Figure 1. Biphasic ionic liquid/hexane system for ethylene polymerization.

Initially, $[C_2\text{-mim}][AlCl_4]$ and $[C_4\text{-mim}][AlCl_4]$ were applied in biphasic ionic liquid/hexane system for ethylene polymerization (Table 1, items 1, 2). The ionic liquid acted as a solvent and, at the same time, immobilizing medium for metallocene catalyst (Cp_2TiCl_2), activated by methylaluminoxane (MAO), $AlEt_3$, or $AlEt_2Cl$ [**H2**].

The polyethylene formed as a white fine powder was gradually passed from the ionic liquid phase to the hexane phase, what was consistent with the idea of biphasic catalysis [15-20]. This allowed the simple separation of the high-purity polymer by decanting, because both the catalyst and the activator remained in the ionic liquid phase. With the extended polymerization time, the amount of PE obtained was gradually increased, which proved that the catalytic system was very stable. Moreover, reuse of the ionic liquid phase in subsequent reaction cycles increases the efficiency of the process.

Table 1. Ionic liquid applied in biphasic ethylene polymerization

No.	Structure	Name	Abbreviation
1		1-*n*-ethyl-3-methylimidazolium tetrachloroaluminate	[C_2-mim][$AlCl_4$]
2		1-*n*-butyl-3-methylimidazolium tetrachloroaluminate	[C_4-mim][$AlCl_4$]
3		1-*n*-hexyl-3-methylimidazolium tetrachloroaluminate	[C_6-mim][$AlCl_4$]
4		1-*n*-octyl-3-methylimidazolium tetrachloroaluminate	[C_8-mim][$AlCl_4$]
5		1-benzyl-3-methylimidazolium tetrachloroaluminate	[Bzl-mim][$AlCl_4$]
6		1-(phenylethyl)-3-methylimidazolium tetrachloroaluminate	[Ph-C_2-mim][$AlCl_4$]
7		1-*n*-butyl-4-methylpyridinium tetrachloroaluminate	[C_4-4-mpy][$AlCl_4$]
8		1-*n*-hexyl-4-methylpyridinium tetrachloroaluminate	[C_6-4-mpy][$AlCl_4$]
9		1-*n*-octyl-4-methylpyridinium tetrachloroaluminate	[C_8-4-mpy][$AlCl_4$]
10		1-*n*-octyl-3-methylpyridinium tetrachloroaluminate	[C_8-3-mpy][$AlCl_4$]
11		1-*n*-butylpyridinium tetrachloroaluminate	[C_4-py][$AlCl_4$]
12		1-*n*-hexylpyridinium tetrachloroaluminate	[C_6-py][$AlCl_4$]
13		1-*n*-octylpyridinium tetrachloroaluminate	[C_8-py][$AlCl_4$]

By the application of the studied biphasic systems, it is possible to withdraw not only the commonly used aromatic solvent, but also MAO as metallocene activator and replacing it with traditional alkylaluminum compounds. The best in this respect was $AlEtCl_2$, which provided the highest system activity [**H3**]. Another benefit was the lack of the reactor fouling phenomenon, which is a problem in reactions involving homogeneous metallocene catalysts. The results showed that the length of alkyl chain at imidazolium cation has a significant influence both on the polymerization performance and the PE properties.

Of these two ionic liquids used, 1-*n*-butyl-3-methylimidazolium chloroaluminate with longer *n*-alkyl substituted was definitely a better medium for the Cp_2TiCl_2 catalyst. Therefore, chloroaluminate ionic liquids with 1-*n*-hexyl-3-methylimidazolium [C_6-mim] and 1-*n*-octyl-3-methylimidazolium [C_8-mim] cation were used for the immobilization of metallocene (Table 1, items 3 and 4) [**H4**]. Irrespective of the type of ionic liquid used, the biphasic polymerization was carried out using relatively small amounts of alkylaluminum compound ($Al/Ti \leq 200$ mol/mol). An optimal mole ratio of activator/catalyst was observed, giving the best performance, i.e. the highest yield and highest amount of product obtained in the hexane phase. In general, the longer alkyl chain at the imidazolium cation the larger amounts of activator needed to ensure maximum process. However, longer alkyl chain allows obtaining more PE product in the hexane phase. This was related to the very important physical properties of ionic liquids, density and viscosity, which have a critical impact on the dispersion of the ionic liquid phase in the hexane phase and thus the availability of the monomer to the active center and the transfer of the polyethylene from the ionic liquid to the hexane phase. Longer alkyl chain on the imidazolium ring reduces the density and increases the viscosity of the ionic liquid phase. Amongst the studied ionic liquids, application of [C_8-mim][$AlCl_4$] enabled to obtained almost all polyethylene in the hexane phase, maintaining a satisfactory yield. Prolongation of reaction time and greater volume of the ionic liquid phase also contributed to an increase in reaction efficiency. The polyethylene obtained in the hexane phase was a linear polymer with a relatively low average molar mass (M_w of 60 000 to 160 000 g/mol) and a melting point (about 133 °C) typical for HDPE obtained using homogeneous metallocene catalysts. However, this PE also had the characteristics of the product obtained using heterogeneous metallocene catalysts, first of all the broader molecular weight distribution (M_w/M_n of about 6) and a high bulk density (more than 500 g/dm^3), which strictly depended on the type of ionic liquid used and increased with the lengthening of alkyl chain at the imidazolium cation. The novelty was a high crystallinity degree of PE (82 to 89%), determined by the Differential Scanning Calorimetry

(DSC) method. In summary, the results confirmed that even a slight modification of the structure of imidazolium ionic liquid by altering the length of the alkyl substituents at the cation significantly affected the polymerization process and allowed for the change of selected polyethylene properties.

A further modification of the imidazolium cation was made by converting the *n*-alkyl group to an aralkyl (benzyl or phenylethyl) group (Table 1, items 5 and 6) [**H5**, **H6**]. It was assumed that the aromatic substituent, by the donor-acceptor interaction with the alkyl-aluminum activator, could affect the acidity of the chloroaluminate ionic liquids as well as participate in the formation of active sites. Such ionic liquids were not applied extensively, although they have higher thermal stability compared to imidazolium analogue with *n*-alkyl substituents [41], and thus, a potential usability in high temperature processes. Synthesized chloroaluminate ionic liquids, 1-benzyl-3-methylimidazolium [Bzl-mim][$AlCl_4$] and 1-(2-phenylethyl)-3-methylimidazolium [Ph-C_2-mim][$AlCl_4$], were crystalline solids at temperature below 40 °C. Thus, the optimum temperature had to be determined for each reaction conducted in these ionic liquids. It was important to take into account the fact that the catalytic activity of titanocene strictly depends on the reaction temperature. In homogeneous systems, polymerization performed at temperature higher than 50 °C results in gradual deactivation of the titanocene catalyst, which considerably decreases the reaction yield [42, 43]. The efficiency of biphasic ethylene polymerization using the aralkyl ionic liquids as the immobilizing medium for the Cp_2TiCl_2 catalyst activated with $AlEtCl_2$ or $AlEt_2Cl$ was influenced not only by the type of ionic liquid used, but also the type and amount of alkylaluminum activator applied. Although, the differences in the structure of aralkyl ionic liquids are small, the immobilization of the catalyst in [$PhCl_2$][$AlCl_4$] allowed for much better results. The highest amount of PE was obtained from the biphasic systems studied so far. However, the polymer remained mostly in the ionic liquid phase. Undoubtedly, the reason for the difficult mass transfer was the high viscosity and density of the ionic liquids, far exceeding those of the previously studied *n*-alkyl substituted analogues. High viscosity, despite a decrease with increasing temperature, significantly reduced the transfer of polymer to the hexane phase. On the other hand, slightly lower density of [Ph-C_2-mim][$AlCl_4$] compared to [Bzl-mim][$AlCl_4$] allowed for better dispersion in the hexane phase, which consequently enhanced monomer access to the active center and resulted in higher catalytic activity of the system. Extended of the reaction time and reuse of the ionic liquid phase generally resulted in the better process performance. The type and amount of alkylaluminum activator are very important factors, which influence the polymerization process with 1-aralkyl-3-methylimidazolium chloroaluminate. As with 1-*n*-alkyl-3-methylimidazolium systems, an optimal mole ratio of activator/catalyst was observed, at which the highest activity of the investigated systems was obtained. The type of alkylaluminum activator had also a considerable effect on the transfer of synthesized polyethylene from the ionic liquid phase to the hexane phase, which is important in biphasic systems. This was especially evident in the [Ph-C_2-mim][$AlCl_4$]/hexane systems, for which the activation of titanocene catalyst by $AlEt_2Cl$ resulted in the accumulation of polyethylene mainly in the hexane phase, irrespective of the amount of activator used. In contrast, when $AlEtCl_2$ was applied, the PE remained in the ionic liquid phase, despite the significantly higher reaction yield. Therefore, it can be suggested that relatively small amounts of alkylaluminum compounds acted not only as activator of titanocene catalyst, but also participated in the formation of chloroethylaluminate anions by reacting with chloroaluminate ionic liquid anions. This in turn has a direct effect on the properties of ionic liquids, especially their acid-base properties [16, 26].

An indispensable condition for polymerization involving chloroaluminate ionic liquids is to provide a weakly acidic reaction medium that is required to form an active catalyst precursor form [36]. The method of regulating the acidic nature of the chloroaluminate ionic liquid is to add appropriate amounts of $AlCl_3$ to the cation chloride substrate. However, an excess of $AlCl_3$ may lead to the creation of acidic $Al_2Cl_7^-$ anions, which contribute to the inactivation of $Cp_2Ti(AlCl_4)_2$ and $Cp_2TiCl(Al_2Cl_7)$ complexes in the polymerization. Also, introduction of $AlEtCl_2$ or $AlEt_2Cl$ contributes to the creation of different types of anions: $AlEtCl_3^-$, $Al_2EtCl_6^-$, $Al_2Et_2Cl_5^-$ and $Al_3EtCl_9^-$ [37, 39]. The optimum conditions for the polyreaction result from the proper amount and type of the resulting anions. Too high amount $AlCl_4^-$ or $AlEtCl_3^-$ (neutral ions) as well as $Al_2Cl_7^-$ or $Al_2EtCl_6^-$ (acidic ions) cause a reduction in the process efficiency. Thus, maintaining the appropriate ratio between different type of the anions by the optimum catalyst/activator molar ratio can provide not only a proper reduction of the titanium compound, but also a suitable polymerization environment. Thus, chloroaluminate ionic liquids were not only a reaction medium that immobilized the titanocene catalyst, but also participated in the formation of catalytic active center [**H5**].

The polyethylene obtained with the 1-aralkyl-3-methylimidazolium chloroaluminate ionic liquids was characterized by slightly lower melting point, crystallinity degree and molecular weight than those obtained with 1-*n*-alkyl-3-methylimidazolium ionic liquids. They differed mainly due to the structure of cation and the type and concentration of the alkylaluminum activator. The reaction temperature, which determines the polymerization efficiency, did not significantly affect the properties of the product. However, the polyethylene had favorable morphological properties; high bulk density and very regular spherical shape of granules. The last feature was obtained in biphasic ionic liquid/hexane systems for the first time, which was probably due to noncovalent interactions with aromatic ring substituents in the nonpolar aralkyl ionic regions (Figure 2). It should be noticed that this type of morphology together with the increase in bulk density and polymer molecular weight with polymerization time are characteristic of the polymer obtained with organometallic solid-carrier catalysts [44, 45], which confirms that the ionic liquid is a specific carrier for titanocene catalyst.

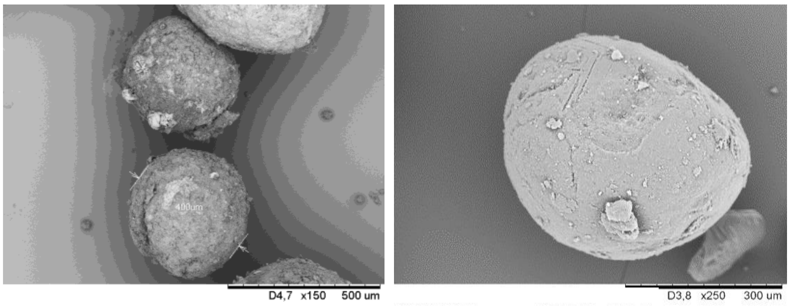


Fig. 2 SEM image of polyethylene obtained using [Ph-C_2-mim][$AlCl_4$]/hexane system.

A considerable decrease of M_w values with an increase of amount of activator in reaction medium was attributed to the involvement of alkylaluminum compound in the polymer chain terminating reaction [**H5**], which is not typical for metallocene catalyst polymerization, where the macromolecule growth is usually terminated by elimination of β-hydrogen [46, 47].

Because of the physical properties of 1-aralkyl-3-methylimidazolium ionic liquids, their use in biphasic polymerization required reaction temperature above 40 °C, which may limit their wider application. Undoubtedly, high viscosity was a disadvantage, also limiting product transfer between phases. The simplest method of reducing the viscosity of ionic liquids is to add a small amount of appropriately selected co-solvent [48]. The most advantageous solution was to add another ionic liquid with a much lower viscosity. In work [**H6**] a mixture of [Ph-C_2-mim][$AlCl_4$] was used with commercially available and relatively inexpensive liquid [C_4-mim][$AlCl_4$], which was one of the most effective specific medium of titanocene catalyst in ethylene polymerization carried at temperature 30 °C [**H2-H4**]. The use of a mixture of ionic liquids enabled the polymerization to proceed at 30 °C, despite the presence of [Ph-C_2-mim][$AlCl_4$]. Regardless of the type and amount of alkylaluminum activator ($AlEtCl_2$ or $AlEt_2Cl$), it was possible to achieve higher yields in biphasic ethylene polymerization, compared to the process carried in single ionic liquid [C_4-mim][$AlCl_4$] or [Ph-C_2-mim][$AlCl_4$]. Other advantages were the easy separation of phases and the obtaining of polyethylene mainly in the hexane phase. Undoubtedly, this was related to the viscosity and density of the ionic liquid mixture. These parameters have reached intermediate values in relation to those determined for particular liquids. By using a mixed phase of the ionic liquid in three consecutive reaction cycles, the catalytic activity exceeded 550 kg PE $(molTi \cdot h)^{-1}$ and was the highest in the biphasic ethylene polymerization achieved so far. The polyethylene obtained in the hexane phase, regardless of the type of activator, was a linear polymer with a similar melting temperature and crystallinity degree, slightly lower as compared the corresponding values obtained for the product synthesized with one type of ionic liquid. It was also characterized by very high bulk density up to 520 g/dm^3 and the irregular shape of the granules. The novelty was bimodal and relatively broad molecular weight distribution (M_w/M_n) PE, suggesting the share of individual ionic liquids in the mixture into the formation of different active sites. This was confirmed by the morphological characteristics of the polymer. The particle size distribution of polyethylene obtained by the mixture of ionic liquids [Ph-C_2-mim][$AlCl_4$] and [C_4-mim][$AlCl_4$] indicated the presence of two dominant PE fractions of different sizes. In contrast, in the case of polymers synthesized in systems with one ionic liquid, the analyzed particle size distribution was clearly monomodal. This once again confirms the contribution of the liquid to the formation of the catalytic center by the appropriate selection of chloroaluminate anions [**H5**] and imidazolium cations [**H6**].

In further studies on the role of the ionic liquid structure in the biphasic ethylene polymerization, it was decided to apply pyridinium cation instead of imidazolium, and thus, by modifying the structure, i.e. changing number, type and position of the substituents on the ring, differentiates ionic liquid properties (Table 1, items 7-13). The reason of using this type of ionic liquid was also the need to supplement very few literature references for their use in oligomerization or olefin polymerization [37, 49, 50]. In the biphasic ethylene polymerization catalyzed by Cp_2TiCl_2 and activated with $AlEtCl_2$ or $AlEt_2Cl$, a number of synthesized dialkylpyridinium (1-*n*-alkyl-methylpyridinium) chloroaluminate ionic liquid were applied: 1-*n*-octyl-3-methylpyridinium tetrachloroaluminate ([C_8-3-mpy][$AlCl_4$]), 1-*n*-octyl-4-methylpyridinium tetrachloroaluminate ([C_8-4-mpy][$AlCl_4$]), 1-*n*-butyl-4-methylpyridinium tetrachloroaluminate ([C_4-4-mpy][$AlCl_4$]), and 1-*n*-hexyl-4-methylpyridinium tetrachloroaluminate ([C_6-4-mpy][$AlCl_4$]) (Table 1, items 7-10) [**H7**, **H8**]. In the first stage of the study, the effectiveness of biphasic polymerization with [C_8-3-mpy][$AlCl_4$] and [C_8-4-mpy][$AlCl_4$], differing in position of alkyl substituent, were compared with the results obtained for imidazolium analogue [C_8-mim][$AlCl_4$]. It was found that the use of pyridinium ionic liquids leads to an increase of the total process yield, regardless of the amount of $AlEtCl_2$ activator of titanocene catalyst. It was particularly advantageous to use the [C_8-4-mpy][$AlCl_4$] ionic liquid containing substituents in the *para* position [**H7**]. Also, the length of the alkyl substituent in the pyridinium cation had an effect on the polymerization yield. Among the used 1-*n*-alkyl-4-methylpyridinium ionic liquids, [C_n-4-mpy][$AlCl_4$], where C_n is: *n*-butyl, *n*-hexyl or *n*-octyl, the highest activity reached in the [C_4-4-mpy][$AlCl_4$] medium [**H8**]. Although higher yield of polyethylene was obtained in the pyridinium systems, compared to the imidazolium analogues, the problem was a significant amount of the product in the ionic liquid phase resulting from limited mass transfer. Undoubtedly, this unfavorable effect was caused by the high viscosity of the ionic liquids, which increased with the length of the *n*-alkyl substituent as well as its position at the pyridinium ring ([C_8-3-mpy][$AlCl_4$] had a significantly higher viscosity than [C_8-4-mpy][$AlCl_4$]). It also explained the observed differences in activity of the investigated systems. Significant improvements in PE transfer from the ionic liquid phase to the hexane phase was observed with prolongation of reaction time as well as the change of activator, from $AlEtCl_2$ to $AlEt_2Cl$. However, application of $AlEt_2Cl$ resulted in a decrease in system activity.

Determination of selected properties of polyethylene obtained in the biphasic dialkylpyridinium tetrachloroaluminate ionic liquid / hexane systems showed that it possesses properties characteristic for polymer obtained both in homogeneous metallocene systems (low molecular weight) and supported analogues (broad molecular weight distribution, high bulk density). In addition, it was characterized by very high degree of crystallinity, unusual for PE, as determined by the DSC method (up to 98%).

In order to limit the unfavorable effects of the high viscosity of dialkylpyridinium ionic liquids on the efficiency of biphasic polymerization, their analogues containing one *n*-alkyl substituent on the pyridinium ring were used [**H9**]. It is known that viscosity decreases with decreasing number of substituents at the cation ring [51]. A series of synthesized 1-*n*-alkylpyridinium chloroaluminate [Cn-py][$AlCl_4$], where Cn is *n*-butyl, *n*-hexyl or *n*-octyl group, was used as the immobilizing medium for the Cp_2TiCl_2 catalyst, activated with $AlEtCl_2$ or $AlEt_2Cl$ (Table 1, items 11-13). It was found that the activity of investigated biphasic systems considerably depends on the type and amount of alkylaluminum activator and the type of monoalkylpyridinium ionic liquid. Almost twice as much yield was obtained when $AlEtCl_2$ instead of $AlEt_2Cl$ was applied. The lower viscosity of monoalkylpyridinium chloroaluminate ionic liquids, in comparison to their dialkylpyridinium analogues, resulted in significant amounts of the product in the hexane phase. The most effective in the ethylene polymerization turned out to be the system, in which the [C4-py][$AlCl_4$] ionic liquid with the shortest alkyl chain at the cation was applied. Not only high activity was achieved, but also PE was primarily gathered in the hexane phase. High stability of the titanocene catalyst immobilized in this ionic liquid was confirmed by the increase of yield with the increase of reaction time as well as the multiple reuse of ionic liquid phase with catalyst. The use of catalytic system with the [C_4-py][$AlCl_4$] ionic liquid, Cp_2TiCl_2 catalyst, and $AlEtCl_2$ activator in three successive reaction cycles resulted in total activity up to 500 kg PE $(mol_{Ti})^{-1}$, which was comparable to that obtained with the best system with imidazolium ionic liquid. Moreover, this system led to high bulk density polyethylene exceeding 600 g/dm^3. It is worth emphasizing that these bulk density values are typical of polyethylene obtained with heterogeneous metallocene catalysts [52-54], while homogeneous systems do not exceed 100 g/dm^3 [55, 56]. PE images made by Scanning Electron Microscope (SEM) confirmed that it has the shape of regular granules, similar in appearance to those obtained in the biphasic systems with 1-aralkyl-3-methylimidazolium chloroaluminate ionic liquids.

The crystallinity degree, which was also very high, was determined using Differential Scanning Calorimetry (DSC), and additionally, by Wide-Angle X-ray Scattering (WAXS) and Positron Annihilation Lifetime Spectroscopy (PALS). The crystallinity degree values determined by the DSC method were slightly higher (about 90%) in comparison to those estimated by WAXS and PALS methods (about 80%), which is due to the specificity of each method. It must be noted, however, that the PE obtained was determined as a high-crystalline polymer, regardless of the method used. Undoubtedly, this unusual feature was the result of the presence of ionic liquid in the reaction medium, in which the polymer was formed. Ionic liquids exhibit a specific nano-structural arrangement where polar regions (domains) containing anions and "heads" of cations are mixed with non-polar regions formed by alkyl side chains [57-59]. The length of the alkyl chain determines the size and order of the non-polar region, and thus, the type of mutual mixing of both domains [57, 59-61]. Such composition of polar and non-polar regions allows ionic liquids to be considered as "two in one" solvents, where each domain (polar or non-polar) is a specific solvent for a given class of compounds. This feature makes possible to use ionic liquids as an olefin polymerization medium for metallocene systems. The polar regions of the ionic liquid effectively maintain both the catalyst and the activator. As a result, it is possible to form cationic transition metal active sites, which catalyze the polymerization reaction. The ethylene monomer is dissolved in the non-polar regions. The mutual mixing of polar and non-polar regions allows the access of non-polar monomer to the polar active centers. The formed polyethylene chains are part of non-polar domain. However, the polar regions of substantially ionic nature, affect the packing of polyethylene chain at the stage of its synthesis. This explains the high crystallinity degree of PE and the small size of resulting crystallites, determined by the WAXS method.

The presented results show that the application of ionic liquid as the specific catalyst medium for the biphasic ethylene polymerization is the promising way to obtain the polymer characterized by unique properties. Particularly advantageous is the use of pyridinium ionic liquids, enabling the production of polyethylene with the characteristics of polymer typically produced using heterogeneous metallocene catalyst on a solid support. The method for obtaining polyethylene with high crystallinity degree and favorable morphological properties in an environment of pyridinium ionic liquid has been patented [**HD1**].

The presented study on the biphasic ethylene polymerization [**H1-H9**] indicates that the proper selection of the ionic liquid phase is the important factor affecting not only the performance of polymerization process, but also the properties of resulting polyethylene. By modification of the cation structure of ionic liquid, it is possible to differentiate physical properties, mainly density and viscosity, which determine substrate and product diffusion, availability of active centers, product transfer between phases, phase separation upon the completion of reaction as well as the adhesion of product to the apparatus, and thus the process cost.

It was observed during the experiments that the purity and the method of synthesis of the chloroaluminate ionic liquids had a significant effect on their physicochemical properties. This is primarily due to the sensitivity of chloroaluminates to trace amounts of moisture, which, due to changes of chemical structure, is particularly responsible for falsifying density and viscosity values. It is therefore necessary to synthesize this type of liquid in completely anhydrous conditions under an inert gas atmosphere using the Schlenk technique. The series of chloroaluminate ionic liquids of high-purity, previously used in the biphasic systems, was the material for accurate viscosity and density measurements that were conducted under inert conditions at the temperature range from 20 to 70 °C [**H10**]. The influence of structure of cation as well as the type, length and position of *n*-alkyl substituent at the ionic liquid cation, the type of chloroaluminate anions, the mixture of ionic liquids, and the addition of solvents (hexane and toluene) on the viscosity and density of ionic liquid were investigated. In accordance with the general trend observed for ionic liquids, density decreased and viscosity increased, with increasing temperatures [62, 63] and cation size [64]. The increase of length of alkyl substituent in the cation and its position *meta* relative to the methyl group resulted in a decrease of density and viscosity. A similar effect was observed after mixing two types of ionic liquids as well as by adding the aliphatic (hexane) or aromatic (toluene) solvent. Other dependencies were noted after the introduction of additional $AlCl_3$ to the neutral tetrachloroaluminate ionic liquid. In these conditions, $Al_2Cl_7^-$ anions have appeared which are characterized by lower symmetry, better charge distribution compared to $AlCl_4^-$ anions, and increased the molecular weight, which in turn caused the decrease of viscosity and the increase of density of ionic liquids [65]. Presented details on these important physical parameters will certainly be useful not only in the design of oligomerization or polymerization reactions in biphasic systems, but also in many other processes involving chloroaluminate ionic liquids.

Ethylene polymerization using SIL catalyst systems

The biphasic systems, in which one of the phases was a properly selected ionic liquid acting as a specific carrier for organometallic catalyst, has proved to be an interesting alternative to traditional heterogeneous systems for olefin polymerization. The specificity of the ionic liquids allowed controlling the polymerization process and the selected properties of polyethylene. However, this type of system was characterized by a relatively low use of catalyst due to limited contact between the phases. In addition, the high viscosity of ionic liquids hindered substrate diffusion into the active sites and limited product transfer between the phases. The biphasic system requires the use of significant amounts of expensive ionic liquids [66, 67]. There is also no possibility of its application in modern technological processes of production of polyolefins in the fluid phase [66, 68, 69].

The concept of *Supported Ionic Liquid* (SIL) is a solution that limits the disadvantages of biphasic systems while maintaining the unique, beneficial effect of ionic liquids on the performance of ethylene polymerization. Such systems, despite their high popularity in organic synthesis, have not been applied in the coordinative polymerization of olefins so far. Therefore, the SIL method was used to synthesize heterogeneous metallocene and postmetallocene catalytic systems for ethylene polymerization (Figure 3) [**H11**].

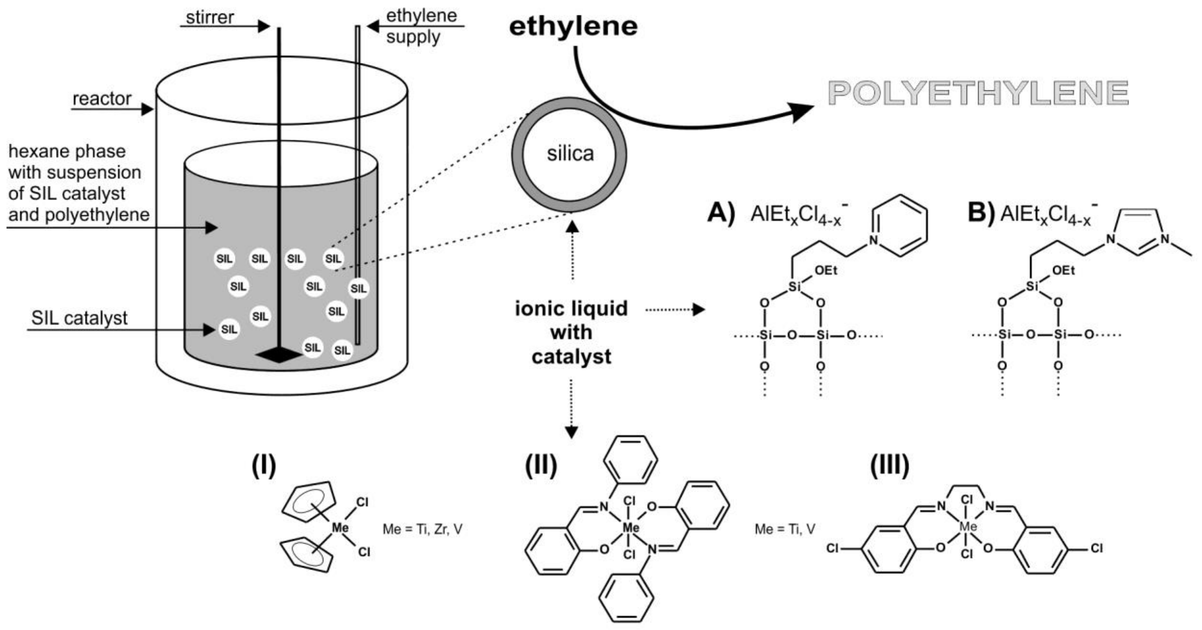


Fig. 3 Scheme of ethylene polymerization using SIL catalyst system.

The following Cp_2TiCl_2 and Cp_2ZrCl_2 as well as bis(phenoxyimine) and salene titanium(IV) complexes (Figure 3 I-III) were immobilized in the 1-[(3-triethoxysilyl)propyl]-3-methylimidazolium ethylchloroaluminate ionic liquid (IL) anchored on a mesoporous amorphous silica surface (Figure 3A).

A thin layer of ionic liquid, covalently anchored on silica, as confirmed by FTIR, TGA, ^{29}Si NMR, SEM, BET, and elemental analysis (EA) methods, led to a change in morphology of silica support. The ionic liquid acted as an immobilizing agent for catalyst, which prevents direct interaction with the surface of silica support. In this way, the catalyst retains its homogeneous character. The applied SIL catalysts, activated by $AlEt_2Cl$, $AlEtCl_2$, or MAO, showed differentiated activity. The best system, SIL/Cp_2TiCl_2/$AlEt_2Cl$, enabled to obtain 3.6 tons of $\mathrm{PE}\cdot(\mathrm{mol_{Ti}}\cdot 0{,}5\ \mathrm{h})^{-1}$. Its efficiency far outweighed that achieved with the Cp_2TiCl_2 catalyst supported directly on silica, without the presence of ionic liquid, as well as those with the most effective biphasic ionic liquid systems. As with typical supported catalysts, the activity of studied SIL systems increased with reaction time, to about 5.4 tons PE $(\mathrm{molTi}\cdot 1.5\ \mathrm{h})^{-1}$, indicating its high stability. The polyethylene was a linear polymer with an average molecular weight (M_w) of up to 600 000 g/mol, much higher than for the PE obtained in the biphasic systems. In addition, it was characterized by the narrow and monomodal molecular weight distribution, which demonstrates the lack of direct interaction of silica support with the catalytic system. The high melting point and crystallinity degree typical was for HDPE. Regular, porous polyethylene granules exhibited similarity to the morphology of particles of SIL catalytic system, which may indicate replication process, which is a common and desirable phenomenon in the case of organometallic supported catalysts for olefin polymerization [70, 71].

The ionic liquid, as a component of the supported catalyst for ethylene polymerization, enhanced its activity, eliminated the disadvantages associated with conducting the process in biphasic systems, and opened up the possibility of application of SIL systems in fluidized bed processes. The method of polyethylene production by using the supported catalysts with ionic liquids is the subject of patent [**HD2**].

SIL vanadium systems

The SIL method allowed the use of both metallocene and postmetallocene complexes, not only with titanium but also zirconium as well as vanadium. This was not provided by the previously discussed biphasic systems. Especially advantageous was the ethylene polymerization using the SIL systems with vanadium(IV) complexes (Figure 3 I, III): Cp_2VCl_2 and VCl_2(saleneCl$_2$) activated by $AlEt_2Cl$ or $AlEtCl_2$. Monodisperse polyethylene with very high molar mass and untypical fiber morphology was obtained [**H12**]. The SIL/vanadium catalysts were significantly more active and stable compared to their homogeneous analogues. The highest activity of the SIL/Cp_2VCl_2 and SIL/VCl_2(saleneCl$_2$) systems (0.5 ton of PE $(mol_V\ h)^{-1}$ and 2 tons of PE $(mol_V \cdot 0.5h)^{-1}$ were obtained using $AlEt_2Cl$ as activator. The application of $AlEtCl_2$ or MAO resulted in a marked decrease in catalyst efficiency. Undoubtedly, increased stability during the reaction is due to the presence of chloroaluminate ionic liquid, which limits the reduction of vanadium to its inactive forms [72-76]. On the other hand, an appropriately selected amount of chloralkylaluminum compound provided the formation of anions that optimize the environment for polymerization. By using $AlEt_2Cl$ or $AlEtCl_2$, the polyethylene obtained from the SIL systems was characterized by the high molecular weight ($M_w > 1$ million g/mol), narrow and monomodal molecular weight distribution ($M_w/M_n \leq 2.5$), which confirmed the homogeneity of active centers typical of homogeneous catalysts, and had an atypical form of fibers. It is noteworthy that the use of MAO activator had a negative effect on PE properties and caused that the polymer had a form of very irregular granules. The fibrous nature of polymer, confirmed by DSC, WAXS, FTIR and SEM methods, depends not only on the presence of ionic liquid in the vanadium SIL system, but also on the type of activator and the appropriate reaction parameters. As a result, the polyethylene obtained had atypical properties: high molecular weight resulting from the presence of heterogeneous catalyst, low dispersion degree due to the homogeneous nature of catalyst immobilized in the ionic liquid, and fiber morphology. The production of high molecular weight polyethylene in the form of fibers, directly during the reaction, was claimed in patent [**HD3**].

Silica supports in the SIL system

Despite very interesting features, the amount of PE produced with the vanadium SIL systems was relatively small. Therefore, it was necessary to change the methodology of their synthesis. For this purpose, the SIL/Cp_2VCl_2 systems were obtained with three types of silica that were modified by ionic liquid with 1-[(3-triethoxysilyl)propyl]pyridine cation (Figure 3B) [**H13**], not applied so far in supported organometallic catalyst system for polymerization and oligomerization. Previous studies of ethylene polymerization in a biphasic system with using pyridinium chloroaluminates have shown that these ionic liquids can be very effective medium for titanocene catalyst and favor the formation of high crystalline PE [**H8**, **H9**]. To produce the appropriate amount and type of alkylchloroaluminate anions in the reaction medium, fixed proportions of $AlCl_3$ and $AlEtCl_2$ or $AlEt_2Cl$ was used. It was found that the SIL systems with pyridinium ionic liquid exhibited higher activity as compared to analogous systems, in which vanadocene was anchored directly onto silica modified with alkylaluminum compound without the presence of ionic liquid. The best results were provided by silica with very regular spherical morphology, a large surface area, and small and narrow pores. On this support, the covalently anchored thin layer of ionic liquid effectively blocked the pores and led to the very even distribution of catalyst on its surface, which facilitated monomer access to homogeneously formed active centers. Moreover, the type of alkylaluminum compound determined the type of alkylchloroaluminate anions, which in turn determines the Lewis acidity of reaction medium, which is suitable for the creation of active catalytic sites. The use of mixture of $AlCl_3$ and $AlEt_2Cl$ to produce diethylchloroaluminate anions as well as $AlEtCl_2$ activator for the SIL/Cp_2VCl_2 gave the yield of 2 tons of PE $(mol_V \cdot 0.5h)^{-1}$. A clear increase in reaction efficiency was obtained by using ethyl trichloroacetate (ETA) as re-activator. It prevents the reduction of vanadium to inactive forms and increases the stability and activity of the catalyst (more than 7 tons PE $(mol_V \cdot 0.5h)^{-1}$). The use of both the new silica type and the pyridinium ionic liquid proved to be very beneficial for the efficiency of SIL systems. The characteristic features of resulting polyethylene were maintained: high molecular weight (M_w) up to 1.4 million g/mol typical for homogeneous active sites, narrow molecular weight distribution (M_w/M_n from 1.4 to 1.9), and fibrous morphology. It is also worth mentioning that the PE obtained with typical supported catalyst, without the presence of ionic liquid, generally showed a slightly higher M_w and broader molecular weight distribution ($M_w/M_n \leq 2.5$). The PE morphology depended on the type of silica used, which resulted from the replication of the morphology of the support by the polymer. The use of SIL/Cp_2VCl_2 systems disrupts the replication phenomenon, but contributes to the formation of atypical fibrous structure (Figure 4).

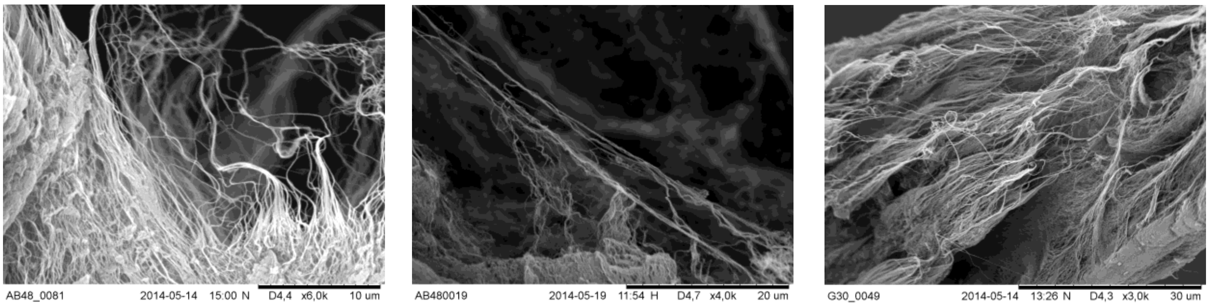


Fig. 4 SEM image of polyethylene obtained using the SIL systems.

SIL systems in co-polymerization

The presented results [**H11-H13**] have shown that SIL systems can successfully be used as an alternative to traditional heterogenization methods of metallocene and postmetallocene catalysts for the ethylene homopolymerization and the resulting polymer have atypical properties. The SIL systems were used for the first time in olefins copolymerization reactions to demonstrate their wider usability. The most effective SIL/Cp_2VCl_2 and SIL/VCl_2(salenCl_2) catalysts were successfully used in the copolymerization of ethylene with cyclic olefin (norbornene) and 1-olefin (1-octene) [**H14**]. The presence of catalytic active sites in the ionic liquid environment did not prevent the incorporation of the larger comonomer units into the polymer chain. The applied SIL systems exhibited higher activity and better comonomer incorporation than analogous homogeneous catalysts as well as heterogeneous systems that are known from the literature. The degree of comonomer incorporation increased linearly with increasing its initial concentration in the reaction medium. The SIL systems, especially SIL/Cp_2VCl_2, have found to be particularly effective in copolymerization of ethylene with norbornene. The properties of copolymers depended on the type of catalyst as well as the type of comonomer and incorporation level of comonomer in copolymer chain. However, their characteristic feature was a relatively narrow molecular weight distribution, which is due to the presence of both the vanadium metal center and the ionic liquid, which results in the formation of single active sites. The presented results open the way for copolymerization of various types (co)monomers using the SIL systems containing different types of ligands and transition metals.

PERSPECTIVES

Current research has been extended to include the synthesis of catalytic complexes. For this purpose, heterocyclic oxazoline ligands have been used, and in the longer term, the synthesis of less-studied oxazoles is also planned. Synthesis of complexes also allows for the extension of research into other transition metals, not only titanium, zirconium and vanadium, but also of high interest, iron and cobalt, which have attracted considerable interest presently. The resulting complexes will be used in supported or non-supported catalyst systems with ionic liquids for the ethylene (co)polymerization. Current research shows that the use of a new type of catalyst with oxazoline ligands in combination with ionic liquids leads to polymers with atypical and tailored properties. Further research will involve determination not only the activity of the synthesized complexes, but also the physicochemical and mechanical properties of the copolymers obtained. The second direction of scientific activity is the synthesis and investigation of properties of new type of functionalized ionic liquids. Cooperation on the use of obtained liquids in catalytic organic reactions is underway.

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5. Presentation of other scientific achievements

My scientific activity is related to the synthesis of multi-component organometallic catalyst systems and their characteristics in the coordinative reactions of olefins polymerization and copolymerization as well as the characteristics of properties of resulting polymer products. In 1996, under the supervision of Professor Krystyna Czaja, I completed and defended my master's thesis, entitled "*Study of ethylene polymerization catalyzed by system containing vanadium chloride*". After graduation, I was employed at the Department of Chemical Technology and Polymer Chemistry as assistant. At that time, under the supervision of Professor Maria Nowakowska, I conducted research, largely implemented within the framework of the grant promoter, in the field of the synthesis of Ziegler-Natta catalysts and metallocene, mainly zirconocene catalysts for ethylene polymerization. The result was a PhD thesis "*Metallocene catalysts immobilized on a complex magnesium carrier for ethylene polymerization*", which I defended in 2004 with 8 articles in journals located in the JCR database and one chapter in English monograph. After completion of the PhD degree I was employed as adjunct and I started work on the synthesis of organometallic complexes with ionic liquids for ethylene polymerization and the correlation between the structure of obtained catalysts and the course of polyreaction and the properties of polymers obtained. The results of these studies are the basis for the presented achievement. A significant part of the research was financed by two research projects of the Ministry of Science and Higher Education and the National Science Centre, between 2005-2008 and 2009-2012. My research goal could be realized thanks to cooperation with prof. Stanisław Rabiej from the Faculty of Materials, Civil and Environmental Engineering of the University of Bielsko-Biala, prof. Teofil Jesionowski from the Faculty of Chemical Technology of the Poznan University of Technology, Dr Roman Szatanik from the Faculty of Mathematics, Physics and Computer Science from the University of Opole, and dr hab. Małgorzata Rajfur from the Faculty of Natural and Technological from the University of Opole. During this time I continued to work on titanium- and zirconium-magnesium-aluminum catalysts for ethylene polymerization (2 publications). Other research directions were participation in the synthesis of pyrazole derivatives (1 publication) in the Department of Organic Chemistry from the University of Opole, like also in the ionic liquids used in reactions of phenol condensation with ketoesters (1 publication) conducted in cooperation with the Institute of Heavy Organic Synthesis in Kedzierzyn-Kozle, where I practiced for three months.

5.1. Co-authorship of scientific publications

I am the author or co-author of 27 scientific publications, including 21 publications in the journals included in the Journal Citation Reports (JCR), 2 chapters in English monographs and 3 patents. The total impact factor (IF) is 30.916, before the PhD thesis 3.771, after 27.145. The total number of citations of these publications, excluding self-citations according the Web of Science & Scopus is 105, and h-index = 6.

5.2.Co-authorship of national patents

I am co-author of 3 polish patents (**HD1-HD3**).

5.3. Presentation at national and international conferences

The results of my research were presented at 18 international and 20 national conferences in the form of 47 oral presentations and posters. A detailed list of presentations is included in Appendix 6

5.4. Participation in grants:

1. Grant (NCN) No N N209 335337. *Bihpasic ethylene polymerazation using metallocene catalyst immobilized in ionic liquids (Dwufazowa polimeryzacja etylenu wobec katalizatorów metalocenowych immobilizowanych w cieczach jonowych).* (22.10.2009-21.12.2012), project supervisor.
2. Grant (MNiSW) No 3 T09B 003 29. Organometallic catalytic complexes with ionic liquids for ethylene polymerization (*Kompleksowe katalizatory metaloorganiczne z udziałem cieczy jonowych do polimeryzacji etylenu).* (25.10.2005-24.04.2008), project supervisor.
3. Grant (KBN) No 3 T09B 076 19. Metallocene catalysts for ethylene polymerization (*Metalocenowe katalizatory polimeryzacji etylenu).* (01.10.2000-30.09.2003), main performer of the project (prof. Maria Nowakowska as project supervisor).

5.5. Scientific supervision of PhD students as promoter and auxiliary promoter

In the years 2008-2013 I participated in the research of the PhD student, Katarzyna Dziubek, who completed the PhD thesis entitled "*Biphasic polymerization of ethylene with organometallic catalysts using ionic liquids*", led by prof. Krystyna Czaja.

From June 2016, I will be the auxiliary promoter of PhD thesis entitled *"(Co)polymerization of ethylene with norbornene with organometallic vanadium catalysts using ionic liquids"* prepared by the PhD student, Anna Bihun, led by prof. Krystyna Czaja.

5.6 . Scientific article reviews

Since 2004, at the invitation of editors of international journals in the JCR database, I have made 34 reviews of scientific manuscripts.

5.7. Awards for scientific activity

1. 2004, Rector's Award of the University of Opole for academic achievements
2. 2009, Rector's Award of the University of Opole for organizational, scientific and research activities and research achievements and acquisition of research projects.

5.8. Membership in scientific organizations

Member of the Polish Chemical Society since 1996.

5.9. Didactic activity

My didactic activity is mainly related to the Faculty of Chemistry (formerly the Institute of Chemistry) of the University of Opole and includes lectures, seminars, laboratory exercises and diploma theses.

My achievements include:

- development of program for 10 chemistry courses, I, II and III level of high education,
- participation in the development of the program of study "Modern Materials",
- promoter of 10 master's theses, 2 undergraduate diplomas, and 2 engineering diplomas and supervision of 10 master's thesis,
- technical assistance in one PhD thesis and auxiliary promoter of the second PhD thesis (ongoing).

My didactic activity also concerned the popularization of science among students in primary, lower secondary and upper secondary schools. In the years 2008-2017, in form of 28 lectures and popular science shows, I introduced students of different types of schools with questions of chemistry, primarily plastics. In the year 2014/2015, as part of the project Fascinating World of Science and Technology, I performed 100 lectures with a show entitled *“Identification of the most popular plastics”*, addressed to students (about 12,000) from IV-VI primary schools from the Opole region.

Wioletta
Ochędzan-Siodłak