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**SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS
SUPPORTING THE HABILITATION APPLICATION**

ATTACHMENT 2

Warsaw, 22.02.2017

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1. Information about the Candidate

Name of the candidate

Paweł Filip Horeglad

Education and academic degrees

- M. Sc.** 2001, Master of Science in the field of Chemical Technology,
Faculty of Chemistry, Warsaw University of Technology
- M. Sc. Thesis *Synthesis and structure of aluminum complexes with maltol and 3-hydroxyflavone*
- Supervisor Janusz Lewiński, Ph. D. (currently Professor)
- M. Sc.** 2001, Master of Science with specialization in environmental
engineering and sustainable infrastructure
Division of Water Resources Engineering, Royal Institute of
Technology, Stockholm, Sweden
- M. Sc. Thesis *Deammonification – a new process for treatment of ammonium rich
wastewater*
- Supervisors Prof. Bengt Hultman, Józef Trela, Ph. D.
- Ph. D.** 2006, Doctor of Science in the field of chemistry,
Faculty of Chemistry, Warsaw University of Technology
- Ph. D. Thesis *Modelling of alkoxyaluminum centers in the polymerization of cyclic
esters and olephine oxides*
- Supervisor Prof. Janusz Lewiński, Warsaw University of Technology (currently
Professor)
- Reviewers Prof. Piotr Sobota, University of Wrocław
Prof. Antoni Pietrzykowski, Warsaw University of Technology

Information on employment in scientific institutions

- 03/2006 – 05/2007 Research and Teaching Assistant Professor, Faculty of Chemistry,
Warsaw University of Technology
- 05/2007 – 05/2009 Ingénieur chercheur, Post doctoral fellow in the research group of Dr.
Marinella Mazzanti (currently Prof. École Polytechnique Fédérale de
Lausanne), at Commissariat à l'Energie Atomique, Grenoble, France
- 11/2009 – 09/2013 Independent engineering-technical worker, Post doctoral fellow in the

research group of Prof. Karol Grela, at the Faculty of Chemistry, University of Warsaw.

since 10/2013 Research Assistant Professor, Centre of New Technologies, University of Warsaw (team leader: Organometallic Chemistry Laboratory)

2. Scientific and research activity

Before earning a M. Sc. degree

In 1995r. I graduated from IXIV Secondary School in Warsaw, biology-chemical profile. In the same year I started studies in Chemical Technology at the Faculty of Chemistry, Warsaw University of Technology. After completing the second year of studies I carried out an individual course of study under the supervision of Janusz Lewiński, PhD (currently Professor). The plan of my classes, outside regular program, included, first of all, the subjects concerned with polymer chemistry, including the lecture of Prof. Witold Kuran on the coordination polymerization, which allowed me to learn about different aspects of application of metal based catalysts for the syntheses of polymers. At that time I was also involved in the research work carried by doctor Janusz Lewiński, which included the investigation of synthesis and structure of organoaluminum complexes as well as their activity in selected stoichiometric and catalytic reactions, among others in the polymerization of olefin oxides. Most of the results of my research work were later included in my M. Sc. Thesis. My participation in the research work resulted in co-authorship of one scientific publication (A1) and an oral presentation at Ph. D. seminar on organometallic chemistry (K1). In March 2001, I defended my M. Sc. thesis titled " *Synthesis and structure of aluminum complexes with maltol and 3-hydroxyflavone*".

During master studies at the Faculty of Chemistry, Warsaw University of Technology, after completing the fourth year of studies, I started M. Sc. studies at the Division of Water Resources Engineering, Royal Institute of Technology, Stockholm, Sweden, for which I was granted a one year leave. At that time I took part in the scientific work on the removal of nitrogen from the wastewater in the activated sludge process, carried in the research group of Professor Bengt Hultman. The possibility of the application of deammonification process for the removal of nitrogen from the ammonia rich wastewater became later the topic of my M. Sc. thesis titled: „*Deammonification – a new process for treatment of ammonium rich wastewater*”. My participation in the research work resulted in the co-authorship of one scientific publication (A2).

Before earning a Ph. D. degree

After my return to Poland in October 2001, I started Ph. D. studies at the Faculty of Chemistry, Warsaw University of Technology. The primary topic of my research work, carried under the supervision of Associate Professor Janusz Lewiński, concerned the effect of the structure of aluminum alkoxide complexes on their activity in the polymerization of heterocyclic monomers such as olefin oxides and cyclic esters. The latter resulted in the explanation of the effect of selected elements of the structure of studied complexes on their activity in the Ring-Opening Polymerization (ROP) of heterocyclic monomers. The obtained results have been published in 4 scientific articles (**A3**, **A4**, **A5** i **A7**). Some of the research work was carried by the students - Anna Rola¹ and Katarzyna Wójcik² under my supervision, and described in their M. Sc. theses. The results of my research work, which were presented and discussed in my Ph. D. thesis titled “*Modelling of alkoxyaluminum centers in the polymerization of cyclic esters and olephine oxides*”, were also published in two scientific articles (**A5**, **A7**). The most important achievements described in publications **A5** i **A7** included, in my opinion, the influence of the chelation effect in the case of $[R_2Al(O,X)]_2$ and $[(EDBP)Al(O,X)]_2$ complexes (where O,X represents alkoxide ligands possessing Lewis Base termini; EDBP-H₂ – 2,2' etylidenebis(4,6-di-tert-butylophenol)) on their activity in the polymerization of ϵ -caprolactone (ϵ -CL) and lactide (LA). One of the most important results was an isolation and characterization of the complex formed as a result of the insertion of two molecules of lactide into Al–O bond of the initiator $[R_2Al(O,X)]_2$. At that time it was the first fully characterized product of the lactide insertion into metal-oxygen bond of an initiator (**A7**). On the other hand, the isolation of stable complex (EDBP)AlMe(ϵ -CL) revealed that high Lewis acidity of a coordination center is not a factor decisive for the activity of an initiator/catalyst (**A5**).

Parallely, I worked on the mechanism of epoxide alkylation with trialkylaluminum compounds (**A6**), together with M. Sc. Ewa Tratkiewicz – a Ph. D. student in the research group of Associate Professor Janusz Lewiński. I was also a co-supervisor of M. Sc. student - Anna Grzegdała, who carried her research work on the synthesis, structure and catalytic

¹ A. Rola, M. Sc. thesis (in Polish) „Polimeryzacja tlenku propylenu i tlenku cykloheksenu z wykorzystaniem zdefiniowanych strukturalnie kompleksów alkiloalkoksyglinowych”, Faculty of Chemistry, Warsaw University of Technology, 2005.

² K. Wójcik, M. Sc. thesis (in Polish) „Synteza, budowa i aktywność katalityczna sześciokoordynacyjnych kompleksów glinu w polimeryzacji laktydu”, Faculty of Chemistry, Warsaw University of Technology, 2006.

activity of zinc alkoxides in the polymerization of ϵ -CL, in the research group of Associate Professor Janusz Lewiński.³

After earning a Ph. D. degree

After obtaining the Ph. D. degree, I continued to work in the Department of Catalysis and Organometallic Chemistry, Faculty of Chemistry, Warsaw University of Technology as an assistant professor (adjunct). At that time I carried the research work on the synthesis, structure and activity of six coordinate aluminum alkoxides. I also continued the supervision of the research work of Katarzyna Wójcik, carried within her M. Sc. thesis² on the topic mentioned above.

The results of the research work on the catalytic properties of aluminum alkoxides in the polymerization of heterocyclic monomers inspired me to investigate the applicability of gallium alkoxides as catalysts for the polymerization of cyclic esters, as it was later shown for the controlled and stereoselective polymerization of racemic lactide (*rac*-LA). It should be stressed that until I started the research on the latter complexes, there had been no reports concerning gallium and indium alkoxide based catalysts for the polymerization of cyclic esters. Notably, the several tens of articles concerning the synthesis, structure and activity of mentioned above gallium and indium catalysts in the polymerization of ϵ -caprolactone and lactide,⁴ which have been published since 2008 in the leading chemical scientific journals, shows how new and interesting topic it was. They include also my publications **H1** – **H6**, which are the series of thematically related scientific papers titled „*Dialkylgallium alkoxide complexes – new catalysts for the controlled and stereoselective polymerization of rac-lactide*”, which constitute the achievement described in details in the chapter 3 of this summary of professional accomplishments.

Before completing the research on the applicability of dialkylgallium alkoxide complexes as catalysts for the polymerization of ϵ -CL and LA, I started my post-doctoral training at Commissariat à l'Energie Atomique (CEA Grenoble) in May 2007, in the research group of Dr. Marinella Mazzanti (currently Prof. École Polytechnique Fédérale de Lausanne). Changing the topic of the research work allowed me to face new scientific problems, which had earlier remained unknown to me, as well as to learn new laboratory techniques. During

³ A. Grzegda, M. Sc. thesis (in Polish) „Synteza polimerów biodegradowalnych z zastosowaniem katalizatorów alkoksycynkowych”, Faculty of Chemistry, Warsaw University of Technology, 2003.

⁴ The examples of mentioned complexes are listed in the review - S. Dagorne, M. Normand, E. Kirillov, J-F. Carpentier “Gallium and indium complexes for ring-opening polymerization of cyclic ethers, esters and carbonates” *Coord. Chem. Rev.* **2013**, 257, 1869–1886 – as well as in publications **A20** – **A22**.

my post-doctoral training, the main topic of my research work concerned the synthesis and characterization of uranyl complexes at +5 oxidation state. At the point I started working on the above mentioned project there were only a few such complexes known, in most cases synthesized in the group of Dr. Mazzanti. However, all known UO_2^+ complexes showed a tendency to disproportionate to UO_2^{2+} and U^{4+} species, which was most probably caused by the presence of $\text{UO}_2^+ \dots \text{UO}_2^+$ interactions, as indicated in the literature. The results of my research work allowed me to conclude that elimination of $\text{UO}_2^+ \dots \text{UO}_2^+$ interactions may lead to stable UO_2^+ complexes, both in the solid state and solution (**A8**, **A9**, **A11**). One of the most important results was the isolation of $[\text{UO}_2(\text{salan-}^t\text{Bu}_2)(\text{py})\text{K}]$ ($(\text{H}_2(\text{salan-}^t\text{Bu}_2) = \text{N,N-bis(2-hydroksybenzylo-3,5-di-tert-butyl)-1,2-dimethylaminometan})$, which is the first example of UO_2^+ complex showing no tendency for disproportionation (**A9**, **A11**). Although the use of less sterically hindered salen ligands for the synthesis of UO_2^+ complexes resulted in the $\text{UO}_2^+ \dots \text{UO}_2^+$ interactions leading to the formation of $(\text{UO}_2^+)_4$ clusters, the significant stability of the latter allowed for the isolation of stable uranyl complexes (+5) (**A10**). Noteworthy, partial oxidation of $(\text{UO}_2^+)_4$ species led to the formation of the first cluster built of uranyl cations at +5 and +6 oxidation states - $(\text{UO}_2^+)_3/(\text{UO}_2^{2+})$. Finally, the factors affecting the stability of isolated complexes were discussed in details in following article (**A13**). Parallely to the research on the uranyl complexes at +5 oxidation state, I investigated uranium complexes at low oxidation states, which have been described in publication **A12**.

After returning to Poland in November 2009, I joined the research group of Prof. Karol Grela as a post doc in the TEAM grant titled „N-heterocyclic carbenes as ligands in olefin metathesis and beyond”, and was allowed to conduct my research work independently. At that time I completed my previous research work on the applicability of dialkylgallium alkoxide complexes as catalysts for the polymerization of *rac*-LA (**H1**), as well as extended this research with the studies on the synthesis, structure and catalytic properties of dialkylgallium alkoxide complexes stabilized with N-heterocyclic carbenes (NHCs) (**H2**, **H4** and partially **H5**). Parallely, as a principal investigator of the IUVENTUS PLUS grant, I carried out the research on the influence of Lewis Bases, other than N-heterocyclic carbenes, on the structure of dialkylgallium alkoxides, as well as their activity and stereoselectivity in the polymerization of *rac*-LA (**H3**).

In 2013 I obtained the position of Research Assistant Professor at the Centre of New Technologies, University of Warsaw (CeNT UW), where I could set my own research group as a team leader of Organometallic Chemistry Laboratory. My current research on the effect of strong Lewis bases on the structure of group 13 and 14 metal alkoxides and their catalytic

activity in the polymerization of heterocyclic monomers is carried within SONATA BIS, NCN grant (2013 – 2018). Until now, I have managed to extend the knowledge about the effect of the structure of dialkylgallium and dialkylindium alkoxides with strong Lewis bases on their activity and stereoselectivity in the polymerization of *rac*-LA and other cyclic esters, as well as their applicability for the synthesis of PLA-drug conjugates bearing PLA of various microstructures (A19). Recently, I also carried the research work, within IMPULS, FNP grant (08/2015 – 10/2016) on the direct synthesis of PLA-beta blockers conjugates using dialkylgallium alkoxides. The latter resulted in patent application P2. Publications H1 – H6, which are the series of thematically related scientific papers titled „ *Dialkylgalliumalkoxide complexes – new catalysts for the controlled and stereoselective polymerization of rac-lactide*”, and constitute the achievement described in details in the chapter 3 of this summary of professional accomplishments represent most of my articles published after returning from post-doctoral training in 2009.

3. Identification of achievement under Art. 16 paragraph. 2 of the Act of 14th of March 2003 on academic degrees and academic titles and degrees and title in art (Dz. U. No. 65, item. 595, as amended.)

Title of the achievement (series of thematically related scientific papers)

Dialkylgallium alkoxide complexes – new catalysts for the controlled and stereoselective polymerization of *rac*-lactide

A series of thematically related scientific papers – the list of papers

In parentheses, next to the publication, I have indicated my percentage contribution to each article⁵. Corresponding author has been in each case indicated with asterisk (*).

H1 P. Horeglad*, P. Kruk, J. Pécaut

*"Heteroselective polymerization of *rac*-lactide in the presence of dialkylgallium alkoxides: The effect of Lewis base on polymerization stereoselectivity"*

Organometallics **2010**, 29, 3729–3734; IF₂₀₁₀ = 3.888, IF₂₀₁₅ = 4.186, number of citations - 39⁶

My contribution included: the formulation of the concept of research work and plan of experiments, the laboratory work including synthesis and

⁵ Declaration of the co-authors of publications are included in the attachment 7 of this application.

⁶ From Web of Science, 21.02.2017.

characterization of studied dialkylgallium alkoxide complexes, the determination of the activity of studied complexes in the polymerization of lactide and characterization of obtained polymers. I have written and published the manuscript. I estimate my contribution to be 90%.

H2 P. Horeglad*, G. Szczepaniak, M. Dranka, J. Zachara

„The first facile stereoselectivity switch in the polymerization of rac-lactide - from heteroselective to isoselective dialkylgallium alkoxides with the help of N-heterocyclic carbenes”

Chem. Commun. **2012**, 48, 1171–1173; IF₂₀₁₂ = 6.378, IF₂₀₁₅ = 6.567, number of citations - 48⁶

My contribution included: the formulation of the concept of research work and plan of experiments, the laboratory work including almost all experiments synthesis i.e. the characterization of studied dialkylgallium alkoxide complexes, the determination of the activity of studied complexes in the polymerization of lactide and characterization of obtained polylactide. I have written, co-edited, and published the manuscript. I estimate my contribution to be 80%.

H3 P. Horeglad*, A. Litwińska, G. Z. Żukowska, D. Kubicki, G. Szczepaniak, M. Dranka, J. Zachara

„The influence of organosuperbases on the structure and activity of dialkylgallium alkoxides in the polymerization of rac-lactide: The road to stereo diblock PLA copolymers”

Appl. Organometal. Chem. **2013**, 27, 328–336; IF₂₀₁₃ = 2.017, IF₂₀₁₅ = 2.452, number of citations - 11⁶

My contribution included: the formulation of the concept of research work and plan of experiments, the laboratory work including some experiments (additionally the supervision of M. Sc. student Anna Litwińska). I have written, co-edited, and published the manuscript. I estimate my contribution to be 60%.

This article has been highlighted by Advances in Engineering, Canada (www.advanceseng.com)

H4 P. Horeglad*, O. Ablialimov, G. Szczepaniak, A. M. Dąbrowska, M. Dranka, J. Zachara

„Dialkylgallium complexes with alkoxide and aryloxy ligands possessing N-heterocyclic carbene functionalities: synthesis and structure”

Organometallics **2014**, 33, 100–111; IF₂₀₁₄ = 4.126, IF₂₀₁₅ = 4.186, number of citations - 10⁶

My contribution included: the formulation of the concept of research work and plan of experiments, the laboratory work including some experiments

concerned with the synthesis and characterization of studied complexes (additionally the supervision of B. Sc. student Anna Maria Dąbrowska). I have written, co-edited, and published the manuscript. I estimate my contribution to be 70%.

H5 P. Horeglad*, M. Cybularczyk, B. Trzaskowski, G. Z. Żukowska, M. Dranka, J. Zachara

„Dialkylgallium alkoxides stabilized with N-heterocyclic carbenes: opportunities and limitations for the controlled and stereoselective polymerization of rac-lactide”

Organometallics **2015**, 34, 3480–3496; IF₂₀₁₅ = 4.186, number of citations - 14⁶

My contribution included: the formulation of the concept of research work and plan of experiments, the laboratory work including most experiments concerned with the synthesis and characterization of studied complexes. I have written, co-edited, and published the manuscript. I estimate my contribution to be 70%.

H6 P. Horeglad*, M. Cybularczyk, A. Litwińska, A. M. Dąbrowska, M. Dranka, G. Z. Żukowska, M. Urbańczyk, M. Michalak

„Controlling the stereoselectivity of rac-LA polymerization by chiral recognition induced the formation of homochiral dimeric metal alkoxides”

Polym. Chem. **2016**, 7, 2022–2036; IF₂₀₁₅ = 5.687, number of citations – 3⁶

My contribution included: the formulation of the concept of research work and plan of experiments, the laboratory work including the synthesis and characterization of model complex 3 and supervision of M. Sc. Students Anna Litwińska and Anna Maria Dąbrowska. I have written, co-edited, and published the manuscript. I estimate my contribution to be 60%.

This article has been highlighted on the cover of 11th issue of *Polymer Chemistry* 2016

Aim of the scientific work

Introduction

In the coordination polymerization the structure of metal complexes considerably influences their catalytic properties and the structure of resulting polymers.⁷ That is why besides the catalytic properties itself, interesting from the point of view of a synthesis of new materials, the understanding of the relationship between the structure and the activity of

⁷ W. Kuran “Principles of Coordination Polymerisation” Wiley: Chichester, 2001.

catalysts/catalytic centers is crucial for the rational design of new catalysts and catalytic systems, which can allow for the synthesis of polymers of desired structure and properties.

In the ring-opening polymerization (ROP) of heterocyclic monomers, the research on the catalysts, based on metal alkoxides, for the polymerization of cyclic esters is of high importance.^{4,8} The polymers synthesized with such catalysts possess often interesting properties and a broad spectrum of applications. Polylactide (PLA) – a biodegradable and biocompatible polymer possessing interesting physicochemical properties should be therefore noted.⁹ The properties of PLA and PLA copolymers highly depend on the microstructure of PLA, including tacticity.¹⁰ Besides, PLA can be synthesized from renewable resources which, among others, resulted in naming it nature's polyethylene.¹¹ One of the most interesting methods of the synthesis of PLA is the ring-opening polymerization of lactide with metal complexes, mainly metal alkoxides.^{4,8,10,12} Notably, the structure of complexes/catalytic centers used is decisive for the activity of catalysts, polymerization and the structure of resulting PLA, including: (i) controlled nature of polymerization leading to PLA of desired average molecular weight (M_n) and low dispersity (\mathcal{D}) (indicated often as polydispersity – PDI), (ii) living and immortal character of polymerization, which can allow for synthesis of PLA copolymers and modification of PLA end groups, (iii) stereoselective polymerization of *rac*-LA ((*R**,*R**)-LA) and/or *meso*-LA ((*R,S*)-LA), which allows, among others, the synthesis of PLA stereoisomers of considerably different physicochemical properties. Therefore, over recent 20 years an effort have been made in order to determine the effect of structure of catalysts/initiators of the polymerization of lactide, including metal alkoxide complexes, on their catalytic properties and the microstructure of resulting PLA. In this case it is important to determine both the structure of a catalyst/initiator and catalytic centers, and to find the relationship between the latter and activity and selectivity in the polymerization of lactide. Such an approach has allowed for the better understanding of the polymerization mechanism,

⁸ A. Buchard, C. M. Bakewell, J. Weiner, C. K. Williams "Recent Developments in Catalytic Activation of Renewable Resources for Polymer Synthesis" *Top Organomet. Chem.* **2012**, 39, 175–224, Springer-Verlag Berlin Heidelberg 2012.

⁹ R. A. Auras, L-T. Lim, S. E. M. Selke, H. Tsuji (Ed.), Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications, John Wiley & Sons, Inc., 2010.

¹⁰ M. J. Stanford, A. P. Dove "Stereocontrolled ring-opening polymerisation of lactide" *Chem. Soc. Rev.* **2010**, 39, 486–494.

¹¹ D. J. Cole-Hamilton "Nature's Polyethylene" *Angew. Chem. Int. Ed.* **2010**, 49, 8564 – 8566.

¹² J. Pretula, S. Słomkowski, S. Penczek „Polylactides—Methods of synthesis and characterization" *Advanced Drug Delivery Reviews* **2016**, 107, 3–16.

as well as made it possible to rationally design new catalysts/catalytic systems resulting in a better control of polymerization process, and to synthesize PLA of desired microstructure.

At the time I published my first article on the dialkylgallium alkoxide complexes and their activity in the polymerization of lactide, in 2010, many well defined catalysts capable of polymerizing LA in the controlled and living fashion were known. However, only some well defined catalysts/catalytic centers allowed for the stereoselective polymerization of *rac*-LA, while the effect of the structure of catalysts/catalytic centers on the stereoselective polymerization of *rac*-LA¹⁰, as *meso*-LA,¹³ was intensively studied. In the following years the interest in the latter topic led to the synthesis of catalysts, based on metal complexes, which allowed for the stereoselective polymerization of lactide, mainly *rac*-LA. My research work on the synthesis structure and activity of dialkylgallium alkoxides in the polymerization of *rac*-LA was in line with the latter, and led to the isolation of new catalysts for the stereoselective polymerization of *rac*-LA (**H1**, **H2**, **H3**, **H5** and **H6**), including catalysts which allowed for the synthesis of PLA of unknown microstructure (**H3**). I have also succeeded in the explanation of the effect of structure of selected catalysts on their stereoselectivity.

Results

My earlier research work concerning the activity of dialkylgallium alkoxides ($[R_2AlOR]_2$) in the polymerization of ϵ -caprolactone (ϵ -CL) and racemic lactide (*rac*-LA), carried during my Ph. D. thesis and described in publication **A7**,¹⁴ was an inspiration for the studies whether dialkylgallium alkoxide complexes could be used as a catalysts for the polymerization of lactide. Noteworthy, although aluminum complexes $[Me_2AlOR]_2$ were highly active in the polymerization of ϵ -CL there showed essentially no activity in the polymerization of *rac*-LA at mild conditions up to 40°C, which was due to the strong interaction of growing PLA chains with aluminum. Although, the increase of temperature allowed for the polymerization of *rac*-LA with $[R_2AlOR]_2$, the presence of transesterification reactions resulted in the higher dispersity of resulting PLA, which precluded the stereoselective polymerization of *rac*-LA. At the beginning of my studies on dialkylgallium alkoxides ($[Me_2GaOR]_2$), I expected that the lower Lewis acidity of gallium in the latter case,

¹³ J-C. Buffet, J. Okuda „Initiators for the stereoselective ring-opening polymerization of *meso*-lactide” *Polym. Chem.* **2011**, 2, 2758–2763.

¹⁴ P. Horeglad, Ph. D. thesis (in Polish) „Modelowanie centrów alkoksylinowych w reakcjach polimeryzacji estrów cyklicznych i tlenków olefin”, Wydział Chemiczny Politechniki Warszawskiej, 2005.

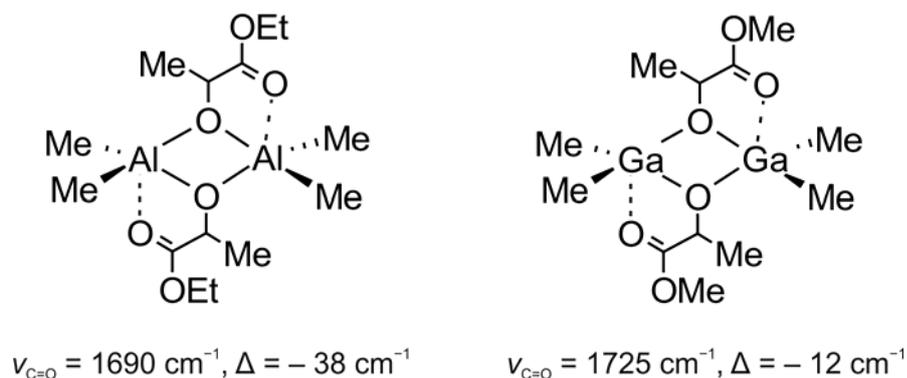
in comparison with aluminum analogues,¹⁵ should result in weaker interaction of growing PLA chains with gallium. I supposed it could enable the polymerization of lactide at mild conditions which could result in controlled and stereoselective polymerization of *rac*-LA. However, when I started my research work no gallium complexes, capable of catalyzing polymerization of lactide were known. Moreover, Chisholm and coworkers had already shown that gallium complexes (BDI)GaCl(OSiMe₃), contrary to zinc complexes – (BDI)ZnOR – active in the polymerization of cyclic esters, showed no activity in the polymerization of either L-lactide (up to 60°C) or propylene oxide.¹⁶ Despite the latter, my studies on the synthesis, structure and catalytic activity of dialkylgallium alkoxides showed that these complexes were active in the polymerization of *rac*-LA, and led to the synthesis first gallium catalysts for the polymerization of *rac*-LA. Dimethylgallium alkoxide complexes ([Me₂Ga(μ-OR)]₂) allowed for the controlled, living and heteroselective polymerization of *rac*-LA (**H1**, **H6**), as well as immortal polymerization of lactide in the case of catalytic systems [Me₂Ga(μ-OR)]₂/ROH (**P2**). In the course of my research I explained the factors controlling the heteroselectivity of dimethylgalliumalkoxides in the presence of Lewis bases (**H6**). Thanks to the use of N-heterocyclic carbenes (NHCs) and organosuperbases for the modification of the structure of dialkylgallium alkoxide complexes I described the first facile switch of stereoselectivity. In the latter cases the reaction of NHCs or organosuperbases such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) with dialkylgallium complexes, which are able to act as heteroselective catalysts ($P_r = 0.5 - 0.85$, where P_r = probability of the formation of *racemo* linkages in PLA), led to the formation of highly active and stereoselective catalytic centers (**H2**, **H3**, **H5**, **P1**), which allowed, among others, the synthesis of PLA of unknown microstructure (**H3**).

At first I isolated, characterized and determined the activity of dimethylgallium alkoxide complexes [Me₂Ga(μ-OR)]₂ in the polymerization of *rac*-LA (**H1**). The use of methyl lactate derivative [Me₂Ga(μ-(S)OCH(Me)CO₂Me)]₂ ([Me₂Ga(*S-melac*)]₂), mimicking the interaction of growing PLA chain with gallium, allowed me to show that the Lewis acidity

¹⁵ C. J. Carmalt, S. J.; King „Gallium(III) and indium(III) alkoxides and aryloxides” *Coord. Chem. Rev.* **2006**, 250, 682–709.

¹⁶ M. H. Chisholm, D. Navarro-Llobet, J. Gallucci „Siloxide and Triflate Gallium(III) Complexes Supported by the BDI Ligand” *Inorg. Chem.* **2001**, 40, 6506-6508.

of dialkylgallium alkoxides is considerably smaller than for aluminum analogues.¹⁷ The latter is shown by the weaker interaction of carbonyl group of methyl lactate ligand with the coordination center in comparison with the analogous aluminum complexes (Scheme 1). It also strongly indicates weaker interaction of growing PLA chain in the case of $[\text{Me}_2\text{Ga}(\mu\text{-O(PLA)})]_2$.



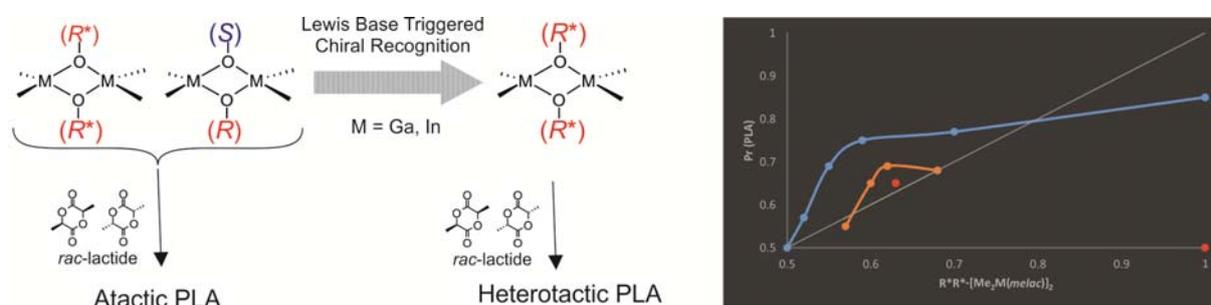
Scheme 1. Comparison of the Lewis acidity of aluminum and gallium for $[\text{Me}_2\text{Al}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Et})]_2$ ¹⁷ i $(S,S)\text{-}[\text{Me}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Me})]_2$ (**H1**). Symbol Δ indicates the difference in the shift of carbonyl group band in FTIR spectroscopy, between respective lactate ligand and complexes shown.

Complexes $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ showed moderate activity in the polymerization *rac*-LA, already at 40°. Under this conditions the polymerization of *rac*-LA was living, which clearly indicated the stability of $[\text{Me}_2\text{Ga}(\mu\text{-O(PLA)})]_2$ centers, where O(PLA) represents the growing PLA chain. Moreover the essential lack of transesterification side reactions allowed for the formation of PLA characterized by very low dispersity, even below 1.1 (**H1**, **H6**). Although these results suggested the possibility of the synthesis of PLA of high average molecular weight (M_n), I did not undertake such studies due to moderate activity of studied complexes. One of the most important results concerned the stereoselective polymerization of *rac*-LA with dialkylgallium alkoxides. While $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ complexes alone did not show any stereoselectivity, in the presence of Lewis bases such as THF or γ -picoline they polymerized *rac*-LA leading to the formation of heterotactic PLA ($P_{\text{r max}} = 0.78$). In this case, I associated the degree of heterotacticity of PLA with the efficiency of coordination of Lewis base to gallium, which was dependent on the donor number of Lewis base as well as on the excess of

¹⁷ J. Lewiński, J. Zachara, I. Justyniak „Structure investigation of a dimethylaluminium derivative of ethyl lactate in the solid state and solution. First evidence for stereoselective association of a dialkylaluminium O,O'-chelate complex” *Chem. Commun.* **1997**, 1519–1520.

Lewis base over $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ (**H1**). Although transesterification reactions could occur at elevated temperatures, $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ complexes were moderately heteroselective even in the case of polymerization of *rac*-LA in melt, at 130°C. However, the origin of heteroselectivity in the case of $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{LB}$ (LB = Lewis base) catalytic systems remained unknown at that time (**H1**).

The effect of Lewis base on the stereoselectivity of catalysts for *rac*-LA polymerization had earlier been observed for other catalysts. However in reported cases the latter was associated with the interaction of Lewis base with the coordination center, which led to the competition of LB and monomer for the coordination to the coordination center and decrease of the polymerization rate as well as the extent of transesterification reactions.¹⁸ However, in the case of the polymerization of *rac*-LA with $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ at 40°C transesterification reactions were not observed. Moreover, on the contrary to previous reports,¹⁸ the addition of Lewis base led to the increase of the polymerization rate, which indicated an unknown effect leading to the heteroselective polymerization of *rac*-LA with metal alkoxides. In order to explain this phenomenon it was necessary to associate the structure of dialkylgallium alkoxide centers active in the heteroselective polymerization of *rac*-LA with their heteroselectivity. The model for the latter centers was *rac*- $[\text{Me}_2\text{Ga}(\text{melac})]_2$ complex, existing in solution as an equimolar mixture of homochiral $(R^*,R^*)\text{-}[\text{Me}_2\text{Ga}(\text{melac})]_2$ and heterochiral $(R,S)\text{-}[\text{Me}_2\text{Ga}(\text{melac})]_2$ dimers (**H6**). As a result of our research described in the article **H6** we have found that the interaction of Lewis base with gallium leads to the excess of homochiral dimers $(R^*,R^*)\text{-}[\text{Me}_2\text{Ga}(\text{melac})]_2$, while the heteroselectivity of dialkylgallium alkoxide centers is related to the excess of homochiral species $(R^*,R^*)\text{-}[\text{Me}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{PLA})]_2$ by nonlinear dependence (Scheme 2). Interestingly, we have observed analogous effects for dialkylindium alkoxides (Scheme 2), which has been discussed in publication **H6**.



¹⁸ M. H. Chisholm, J. Gallucci and K. Phomphrai "Coordination Chemistry and Reactivity of Monomeric Alkoxides and Amides of Magnesium and Zinc Supported by the Diiminato Ligand $\text{CH}(\text{CMeNC}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$. A Comparative Study" *Inorg. Chem.* **2002**, *41*, 2785–2794.

Scheme 2. The effect of Lewis base (LB) on the structure and stereoselectivity of dialkylgallium alkoxide centers for *rac*-[Me₂M(μ-OCH(Me)CO₂PLA)]₂ (M = Ga, In) complexes (left); The dependence of heterotacticity of PLA (*P_r*) on the excess of homochiral dimers (*R**,*R**)-[Me₂M(μ-OCH(Me)CO₂Me)]₂ for the catalytic systems *rac*-[Me₂M(μ-OCH(Me)CO₂PLA)]₂/LB (M = Ga (blue dots), In (orange and red dots) (right). Points are connected with lines only for the clarity of presentation. Red dots represent catalytic systems for which the high tendency for transesterification in the *rac*-LA polymerization has been observed. Figures, originally published in the article **H6** have been used for the preparation of Scheme 2.

The latter represents the first report, which shows that chiral recognition leading to the formation of homochiral metal alkoxide complexes constitute a method for the generation of stereoselective centers in the polymerization of *rac*-LA. In my opinion this method could be extended to the other catalysts for the stereoselective polymerization of chiral monomers. It must be noted that observed non-linear dependence between the excess of homochiral dimers (*R**,*R**)-[Me₂Ga(μ-OCH(Me)CO₂PLA)]₂ and their heteroselectivity in the polymerization of *rac*-LA is only the second such effect concerning the stereoselectivity of homo- and heterochiral dimers in a polymerization.¹⁹ It is also to some extent analogous to the non-linear dependence between the enantiomeric excess of chiral ligand and the enantiomeric excess of a product in the enantioselective organic synthesis.²⁰ It must be stressed that in the latter case the non-linear effect is most of all concerned with a difference between activity and stereoselectivity of homo- and heterochiral dimeric catalytic centers based on metal complexes.

Notably, we have also shown that [Me₂Ga(μ-OR)]₂ complexes can be used for the immortal ring-opening polymerization (*i*ROP²¹) in the presence of alcohols (**P2**). In this case such a possibility is caused by the fact that, contrary to dialkylaluminum alkoxides, [Me₂Ga(μ-OR)]₂ complexes do not show tendency to react with alcohols (R'OH) with evolution of methane. In the case of [Me₂Ga(μ-OR)]₂ the presence of R'OH leads to the exchange of alkoxide ligand and the formation of [Me₂Ga(μ-OR')]₂. The use of e.g. β-blockers (drugs), which are secondary alcohols, in the immortal polymerization of *rac*-LA

¹⁹ K. Nakano, T. Hiyama and K. Nozaki, „Asymmetric amplification in asymmetric alternating copolymerization of cyclohexene oxide and carbon dioxide” *Chem. Commun.*, **2005**, 1871–1873.

²⁰ T. Satyanarayana, S. Abraham and H. B. Kagan “Nonlinear Effects in Asymmetric Catalysis” *Angew. Chem., Int. Ed.*, **2009**, *48*, 456–494.

²¹ N. Ajellal, J-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Helou, V. Poirier, Y. Sarazin, A. Trifonov “Metal-catalyzed immortal ring-opening polymerization of lactones, lactides and cyclic carbonates” *Dalton Trans.* **2010**, *39*, 8363–8376.

with $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$, allowed for the formation of PLA- β -blocker conjugates. Importantly, in this case, the immortal polymerization of *rac*-LA can be heteroselective in the presence of Lewis bases, which could enable the synthesis of PLA- β -blocker conjugates of different stereostructure of PLA. In our patent application we have patented the use of $[\text{R}_2\text{Ga}(\mu\text{-OR})]_2$ catalysts for the immortal ring-opening polymerization of lactide as well as the use of dialkylgallium alkoxides (and dialkylindium alkoxides) for the synthesis of PLA-drug conjugates (**P2**).

The use of N-heterocyclic carbenes (NHCs) as a Lewis base had a very different effect on the structure of dialkylgallium alkoxides and their stereoselectivity in the polymerization of *rac*-LA (**H2**). The reaction of 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes) with $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ resulted in the formation of monomeric complexes $\text{Me}_2\text{Ga}(\text{OR})(\text{SIMes})$, which were highly active in the polymerization of *rac*-LA already at -20°C . At this temperature $\text{Me}_2\text{Ga}(\text{OR})(\text{SIMes})$ complexes catalyzed the polymerization of *rac*-LA in the stereoselective fashion leading to the formation of predominantly isotactic PLA (probability of *meso* linkages - $P_m = 0.78$). It should be stressed that until now $\text{Me}_2\text{Ga}(\text{OR})(\text{SIMes})$ have been one of only a few isoselective complexes highly active at mild conditions.²² They are also one of a few main group metal alkoxides stabilized with NHCs.²³ However, my most important achievement in this case was the observation that the reaction of NHC with $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$, acting as nonselective or heteroselective catalysts in the polymerization of *rac*-LA, leads to the formation of isoselective $\text{Me}_2\text{Ga}(\text{OR})(\text{SIMes})$ complexes, resulting for the first time in the facile switch of stereoselectivity (Scheme 3) (**H2**).

²² In the literature there are only a few reports of mentioned complexes, most of which represents articles published in and after 2014. All examples are listed in the reference 3 of **A22**.

²³ All main group metal alkoxides with NHCs have been cited in publication **A22**. Main group metal complexes with NHC have been presented and discussed in the following reviews: (a) Willans, C. E. „Non-transition metal N-heterocyclic carbene complexes” *Organometallic Chemistry*, The Royal Society of Chemistry: London, 2010, 36, 1–28. (b) Hudnall, T.W., Ugarte, R.A. and Perera, T.A., N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools (2), RSC Catalysis Series (2017) 178.



Scheme 3. The effect of N-heterocyclic carbenes on the structure and stereoselectivity of dimethylgallium alkoxides in the polymerization of *rac*-LA. Scheme 3 is the same as the one published in the article **H2**.

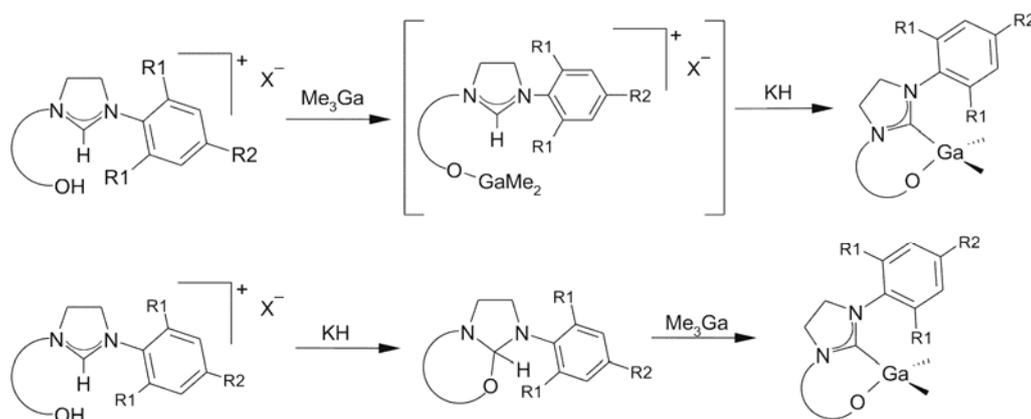
Before the latter result was published in the article **H2**, there had been only one report showing that modification of the structure of a catalyst can lead to the switch of stereoselectivity, from heteroselective to isoselective mode or *vice versa*, in the polymerization of *rac*-LA.²⁴ However, the reports concerning this issue and published after **H2** revealed considerable interest in stereoselectivity switching. With the regard to the latter, our results, described and discussed in publication **H2**, have been noticed, which has been indicated by 42 independent citations of the article **H2** after around 5 years.

Our results, described and discussed in the article **H2** encouraged me to extend the studies concerning dialkylgallium alkoxide complexes, including their catalytic properties in the polymerization of cyclic esters. The results of these studies showed considerable effect of the electronic and steric structure of NHCs on the synthesis and structure of $\text{Me}_2\text{Ga}(\text{OR})(\text{NHC})$ complexes (**H5**). They also showed the effect of NHC on the strength of Ga–C_{NHC} bond, e.g. in the case of $\text{Me}_2\text{Ga}(\text{OR})(\text{SIMes})$ and $\text{Me}_2\text{Ga}(\text{OR})(\text{IMes})$ (IMes - 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) complexes as well as the effect of NHC on the interaction of carbonyl group of methyl lactate ligand, mimicking the growing PLA chain, with gallium. The latter was reflected by the activity of $\text{Me}_2\text{Ga}(\text{OR})(\text{NHC})$ complexes in the polymerization of *rac*-LA (see below). On the other hand, the use of SIPr (1,3-bis-(2,6-diisopropylphenyl)-imidazolin-2-ylidene) of higher steric hindrances in comparison with SIMes and IMes did not allow for the synthesis of $\text{Me}_2\text{Ga}(\text{OR})(\text{SIPr})$. Although the reactivity of $\text{Me}_2\text{Ga}(\text{OR})(\text{NHC})$ (NHC = SIMes, IMes) with Lewis acids such as Me_3Ga and CO_2 led to

²⁴ P. Hornmür, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams “Remarkable Stereocontrol in the Polymerization of Racemic Lactide Using Aluminum Initiators Supported by Tetradentate Aminophenoxide Ligands” *J. Am. Chem. Soc.*, **2004**, 126, 2688–2689.

the reactivity of the latter with NHC with the formation of $\text{Me}_3\text{Ga}(\text{NHC})$ and $(\text{NHC})\text{CO}_2$ adducts, the insertion of lactide occurred in each case exclusively into Ga–O bond of the catalyst. In the case of *rac*-LA polymerization the structure of NHC (SIMes, IMes) had small effect on the high isoselectivity of $\text{Me}_2\text{Ga}(\text{OR})(\text{NHC})$ complexes. On the other hand the effect of NHC on the interaction of growing PLA chain with the coordination center influenced considerably the activity of $\text{Me}_2\text{Ga}(\text{OCH}(\text{Me})\text{C}(\text{O})\text{OMe})(\text{NHC})$ and $\text{Me}_2\text{Ga}(\text{O}(\text{PLA}))(\text{NHC})$ in the polymerization of *rac*-LA as well as average molecular weight (M_n) and dispersity (\mathcal{D}) of resulting PLA, which has been discussed in details in article **H5**. It should be noticed that, despite relatively weak chelate interaction for $\text{Me}_2\text{Ga}(\text{OCH}(\text{Me})\text{CO}_2\text{Me})(\text{NHC})$ (NHC = SIMes, IMes) at room temperature, the lowering of polymerization temperature to -20°C had a considerable effect on the interaction between gallium and C=O group of methyl lactate or growing PLA chain.

With regard to the results concerning the synthesis and structure of $\text{Me}_2\text{Ga}(\text{OR})(\text{NHC})$ complexes (**H5**), it was interesting to investigate the possibility of the synthesis of $\text{Me}_2\text{Ga}(\text{O},\text{C}_{\text{NHC}})$, where $\text{O},\text{C}_{\text{NHC}}$ represents monoanionic alkoxide ligand with NHC termini.²⁵ I supposed such studies should extend the knowledge about this new class of complexes. As a result we isolated a series of $\text{Me}_2\text{Ga}(\text{O},\text{C}_{\text{NHC}})$ using two synthetic methods, including one original strategy, which are presented in the article **H4** (Scheme 4).



Scheme 4. Methods of the synthesis of $\text{Me}_2\text{Ga}(\text{O},\text{C}_{\text{NHC}})$ complexes, where X^- is a halogen anion.

Scheme 4 includes schemes from the article **H4**.

²⁵ S. Hameury, P. de Frémont, P. Braunstein “Metal complexes with oxygen-functionalized NHC ligands: synthesis and applications” *Chem. Soc. Rev.*, **2017**, *46*, 632–733.

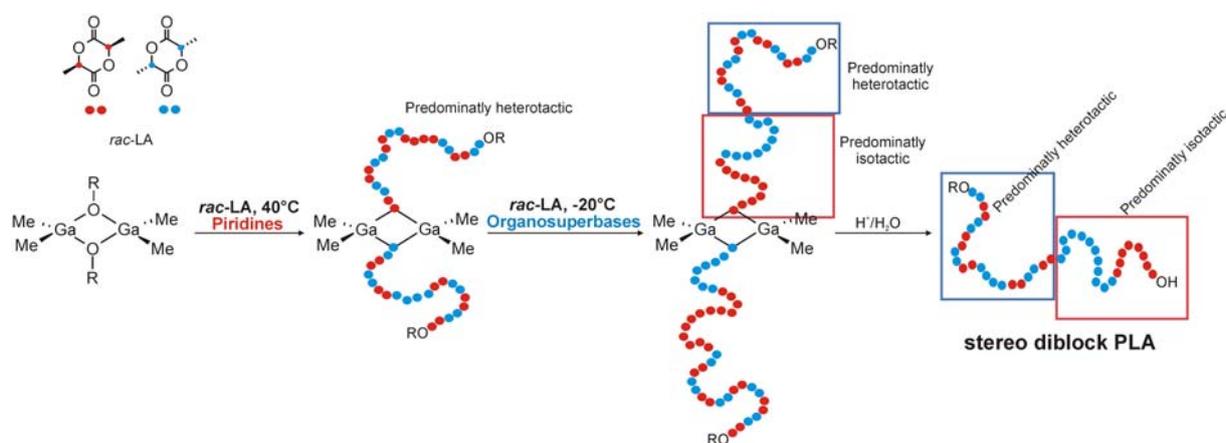
In the article **H4** I discussed in details the effect of O, C_{NHC} on the structure of isolated complexes with an emphasis on the strength of Ga– C_{NHC} bond. Notably, the use of Bond Valence Vector Model (BVV)²⁶ allowed to determine the tension for $Me_2Ga(O, C_{NHC})$, in comparison with $Me_2Ga(OR)(NHC)$, resulting from the presence of O, C_{NHC} chelate ligand as well as the effect of the size of GaO, C_{NHC} ring on the observed tension. It should be stressed, from the point of view of the reactivity of investigated complexes, that reactions of $Me_2Ga(O, C_{NHC})$ with Me_3Ga – a Lewis acid – led to the formation of $Me_2Ga(O, C_{NHC}) \cdot GaMe_3$ adducts as a result of the coordination of Me_3Ga to the alkoxide or aryloxy oxygen of O, C_{NHC} ligand, which was in contrast to the reactivity of $Me_2Ga(OR)(NHC)$ complexes with Lewis acids (see above).

With regard to the results indicating the possibility of easy modification of the stereoselectivity of dialkylgallium complexes, from non selective $[Me_2Ga(\mu-OR)]_2$ or heteroselective e.g. $[Me_2Ga(\mu-OR)]_2/\gamma$ -picoline (**H1**, **H6**) to isoselective $Me_2Ga(OR)(NHC)$ (**H2**, **H5**), I approached the synthesis of stereodiblock PLA built of PLA blocks of different tacticity. I considered the synthesis of polylactide built of predominantly heterotactic PLA and predominantly isotactic PLA, which had had no precedent in the literature, especially interesting. Using NHC, which had allowed for the switch of stereoselectivity, we succeeded in the synthesis of $(PLA\text{-}atactic)_{50}\text{-}b\text{-}(PLA\text{-}isotactic\text{-}P_m\text{-}0.78)_{50}$ in the course of sequential polymerization of *rac*-LA (**H5**). However, we did not succeed in the synthesis of $(PLA\text{-}heterotactic\text{-}P_r\text{-}0.78)_{50}\text{-}b\text{-}(PLA\text{-}isotactic\text{-}P_m\text{-}0.78)_{50}$, which could result from the difficulty in the generation of $Me_2Ga(O(PLA))(NHC)$ catalytic centers in the reaction between $[Me_2Ga(\mu\text{-}OPLA)]_2$ and NHC in the presence of γ -picoline, most probably due reactivity of NHC towards the excess of γ -picoline (**H5**). That is why I became interested in the possibility of the generation of isoselective dialkylgallium alkoxide centers in the reaction between $[Me_2Ga(\mu\text{-}OR)]_2$ and strong Lewis bases other than NHCs. We found that interaction of organosuperbases²⁷ such as *1,8-diazabicyclo[5.4.0]undec-7-ene* (DBU) or *7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene* (MTBD) with gallium of $[Me_2Ga(\mu\text{-}OR)]_2$ led to the formation of highly active and isoselective catalytic centers allowing for the formation of PLA due to insertion of *rac*-LA into Ga–OR bond (**H3**). Although the interaction of neither DBU nor MTBD led to the formation of monomeric $Me_2GaOR(DBU)$ and $Me_2GaOR(MTBD)$ complexes, respectively, the generated catalytic centers allowed, similarly to

²⁶ J. Zachara „Novel Approach to the Concept of Bond-Valence Vectors” *Inorg. Chem.* **2007**, *46*, 9760–9767.

²⁷ T. Ishikawa (Ed.) „Superbases for Organic Synthesis: Guanidines, Amidines Phosphazenes and Related Organocatalysts” Wiley, Chichester, 2009.

$\text{Me}_2\text{Ga}(\text{OR})(\text{NHC})$, for the isoselective polymerization of *rac*-LA already at -20°C . The structure of dialkylgallium alkoxide active centers formed in the case of catalytic systems $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{DBU}$ and $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{MTB}$ was thoroughly discussed in article **H3**. However, the most important for the synthesis of the first example of PLA built of predominantly heterotactic and predominantly isotactic PLA blocks - $(\text{PLA-heterotactic-}P_r = 0.78)_{50}\text{-}b\text{-}(\text{PLA-isotactic-}P_m = 0.79)_{50}$ (Scheme 5) was the fact that DBU or MTBD could be used for the generation of isoselective dialkylgallium alkoxide species. In the publication **H3** we have also shown that the microstructure of synthesized stereodiblock PLA affects its physicochemical properties. Noteworthy, we have also shown, with Prof. Marcin Sobczak and Prof. Ewa Ołędzka from Medical University of Warsaw, that stereostructure of PLA fragment in PLA-drug conjugates affects the drug release properties of the latter (**A19**).



Scheme 5. The sequential polymerization of *rac*-LA, with the use of dialkylgallium alkoxide species, leading to block PLA built of predominantly heterotactic and predominantly isotactic PLA blocks.

Summary and potential use of the results

The results obtained and described in the series of series of thematically related scientific papers **H1** – **H6** concerns the synthesis and structure of dialkylgallium alkoxides as well as their catalytic properties in the polymerization of lactide. In my research work I paid special attention to the effect of the structure of catalysts on their catalytic properties in the polymerization of *rac*-LA. On the other hand, the determination of the effect of PLA microstructure on its physicochemical properties and potential applications has been discussed to a smaller extent, although I have already begun to explore this issue (**A19**, **P2**). The latter is, undoubtedly worth further studies, which could show whether, and to which extent, dialkylgallium catalysts are important from the point of view of applied research.

However, the obtained results focus an attention on dialkylgallium alkoxides from the point of constructing stereoselectivity switches in the polymerization of *rac*-LA. Noteworthy, the studies on switchable catalysts (not only in regard to stereoselectivity) for the ring opening polymerization of heterocyclic monomers have been indicated recently as a frontier research, which could enable the synthesis of new materials concerning both their structure and potential applications.²⁸ In the case of dialkylgallium alkoxides the stereoselectivity switch can be obtained by the synthesis of highly active and stereoselective complexes $R_2GaOR(NHC)$ ($P_{m\ max} = 0.78$) or catalytic systems $[Me_2Ga(\mu-OR)]_2$ /organosuperbases ($P_{m\ max} = 0.78$) due to coordination of NHCs or organosuperbases to $[Me_2Ga(\mu-OR)]_2$, which can polymerize *rac*-LA in non-selective or heteroselective manner in the presence of Lewis bases. Both heteroselective and isoselective dialkylgallium alkoxide centers can be generated in the course of polymerization, which can facilitate/make possible the synthesis of PLA and PLA copolymers of new microstructure and properties. Moreover, $[Me_2Ga(\mu-OR)]_2$ and $[Me_2Ga(\mu-OR)]_2LB$ (where LB = Lewis bases, e.g. pyridines), which allow for the easy tuning of heteroselectivity during *rac*-LA polymerization ($0.5 \leq P_r \leq 0.85$) should be also recognized as stereoselectivity switchable catalysts. Additionally, in this case the results of studies concerning the mechanism of heteroselective polymerization of *rac*-LA with dialkylgallium alkoxides showed a considerable influence of homochiral dimers $(R^*,R^*)-[Me_2Ga(\mu-OCH(Me)CO_2(PLA))]_2$ on the heteroselectivity of dialkylgallium alkoxide catalytic centers. This suggest new method for the design of stereoselective catalysts of not only *rac*-LA, but also other chiral heterocyclic monomers. Moreover it constitutes one of the first reports concerning the effect of diastereomers on the stereoselectivity of *rac*-LA polymerization.

The high activity and isoselectivity of $R_2GaOR(NHC)$ in the polymerization of *rac*-LA has focused my attention on this class of complexes, as well as $Me_2Ga(O,C_{NHC})$ with alkoxide and aryloxide ligands possessing functional groups which are NHCs. It should be stressed that alkoxide and aryloxide gallium complexes with NHCs, which have been isolated in my research group, are the first examples of such complexes within group 13 elements. Noteworthy is also the fact that there are only a few alkoxide and aryloxide complexes of main group metals, which are stabilized with NHCs. It has encouraged me to investigate the effect of $M-C_{NHC}$ on the synthesis, structure and properties of dialkylalkoxide and dialkylaryloxide indium complexes with NHCs (A22).

²⁸ S. M. Guillaume, E. Kirillov, Y. Sarazin, J-F. Carpentier "Beyond stereoselectivity, switchable catalysis: some of the last frontier challenges in ring-opening polymerization of cyclic esters." *Chem. Eur. J.* **2015**, *21*, 7988-8003.

The most important achievements of the series of thematically related scientific papers H1 – H6 include:

- Finding, that gallium alkoxide complexes show activity in the polymerization of lactide (LA), and most importantly, that they catalyze the polymerization of *rac*-LA in the controlled and stereoselective manner.
- Finding, that dialkylgallium alkoxide complexes $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ catalyze the polymerization of *rac*-LA in heteroselective fashion in the presence of Lewis base, while the degree of heteroselectivity, in the range $0.5 < P_T < 0.85$, can be easily modified by the Lewis base (LB) and LB:Ga ratio in the case of catalytic systems $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{LB}$.
- Finding, on the basis of the structure dimeric *rac*- $[\text{Me}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Me})]_2$ complexes, that the formation of homochiral catalytic centers (R^*,R^*)- $[\text{Me}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{R})]_2$ as a result of chiral recognition in the presence of Lewis base is responsible for the heteroselectivity of dialkylgallium alkoxides and may constitute new strategy for the design of stereoselective catalysts of the ROP of *rac*-LA, and probably also other chiral heterocyclic monomers.
- Observation of the first facile stereoselectivity switch by the synthesis of highly active and isoselective $\text{R}_2\text{GaOR}(\text{NHC})$ ($P_{m \max} = 0.78$), as a result the coordination of NHC to $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2$ complexes which polymerize *rac*-LA in non-selective or heteroselective fashion.
- Isolation and characterization of new class of compounds - dialkylgallium alkoxide complexes ($\text{R}_2\text{GaOR}(\text{NHC})$ i $\text{Me}_2\text{Ga}(\text{O},\text{C}_{\text{NHC}})$) - and determination of their catalytic properties in the ring-opening polymerization of lactide and other selected cyclic esters.
- Characterization of gallium species in the case of isoselective catalytic systems $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{organosuperbases}$ in the polymerization of *rac*-LA, which allow for the synthesis of predominantly isotactic PLA ($P_{m \max} = 0.79$).
- Isolation of stereo diblock PLA of previously unknown microstructure - (PLA-heterotactic- $P_T=0.78$)_n-*b*-(PLA-isotactic- $P_m=0.79$)_m – in the course of sequential polymerization of *rac*-LA with the use of heteroselective catalytic systems $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{pyridines}$ and isoselective catalytic systems $[\text{Me}_2\text{Ga}(\mu\text{-OR})]_2/\text{organosuperbases}$.

Future research plans

Mentioned above studies, on the effect of diastereomers of main group metal alkoxides on their catalytic properties in the ring opening polymerization of heterocyclic monomers,

constitute an emerging and interesting topic, which I would like to explore within the research carried in my research group. On the other hand, in the field of organometallic chemistry, I would like to continue the research on the effect of NHC and the character of M–C_{NHC} bond on the structure and properties of main group metal alkoxides and aryloxides with NHC, which constitute new and unexplored class of complexes.

I am also planning to conduct the research on the synthesis of PLA and PLA copolymers of new microstructure and the explanation of the effect of the microstructure of PLA on its properties and application, among others as PLA-drug conjugates. This studies are going to be conducted in the cooperation with Prof. Marcin Sobczak and Prof. Ewa Olędzka from Pharmaceutical Department of Medical University of Warsaw and Dr Andrzej Plichta from Faculty of Chemistry, Warsaw University of Technology.

4. Scientific activity

List of publications

The works are presented in chronological order. The works that are related to the cycle of publications which constitute the Work in accordance with the Act are shown in bold.

The list of scientific articles published before earning a Ph. D. degree:

- A1 J. Lewiński, J. Zachara, **P. Horeglad**, D. Glinka, J. Lipkowski, I. Justyniak „Structural evidence of the epoxide oxygen propensity to double coordination”
Inorg. Chem. **2001**, 40, 6086–6087; IF₂₀₀₁ = 2.946, IF₂₀₁₅ = 4.820, number of citations - 21⁶
- A2 J. Trela, B. Hultman, E. Płaza, **P. Horeglad**, N. C. La Rocca “New methods for biological treatment of supernatant from digested sludge”
In: Wastewater sludge and solid waste management, Report No 9. M. Hopkowicz, B. Hultman, J. Kurbiel, E. Plaza (Editors), TRITA-AMI REPORT 3088, **2001**, p. 113
- A3 J. Lewiński, I. Justyniak, **P. Horeglad**, E. Tratkiewicz, J. Zachara, Z. Ochal „Alkylaluminum alkoxides derived from donor-functionalized alcohols: Factors controlling the formation and redistribution of products”
Organometallics **2004**, 23, 4430–4437; IF₂₀₀₄ = 3.196, IF₂₀₁₅ = 4.186, number of citations – 14⁶
- A4 J. Lewiński, **P. Horeglad**, M. Dranka, I Justyniak „Simple generation of cationic aluminum alkyls and alkoxides based on the pendant arm tridentate Schiff base”
Inorg. Chem. **2004**, 43, 5789–5791; IF₂₀₀₄ = 3.454, IF₂₀₁₅ = 4.820, number of citations - 75⁶
- A5 J. Lewiński, **P. Horeglad**, E. Tratkiewicz, W. Grzenda, J. Lipkowski, E.

Kołodziejczyk „Towards the nature of active sites in polymerization of cyclic esters initiated by aluminium alkoxides: First structurally authenticated aluminium- ϵ -caprolactone complex”

Macromol. Rapid. Commun. **2004**, 25, 1939–1942; IF₂₀₀₄ = 3.366, IF₂₀₁₅ = 4.638, number of citations - 36⁶

- A6 J. Lewiński, **P. Horeglad**, E. Tratkiewicz, I. Justyniak, Z. Ochal „Ring-opening of 2,3-epoxy-1-propanol with R₃Al: Unprecedented regiochemical switching simply achieved by changing alkyl substituents of aluminium reagent”

J. Organomet. Chem. **2005**, 690, 3697–3699; IF₂₀₀₅ = 2.025, IF₂₀₁₅ = 2.336, number of citations - 5⁶

- A7 J. Lewiński, **P. Horeglad**, K. Wójcik, I. Justyniak „Chelation effect in polymerization of cyclic esters by metal alkoxides: Structure characterization of the intermediate formed by primary insertion of lactide into the Al-OR bond of an organometallic initiator”

Organometallics **2005**, 24, 4588–4593; IF₂₀₀₅ = 3.473, IF₂₀₁₅ = 4.186, number of citations – 57⁶

The list of scientific articles published after earning a Ph. D. degree:

- A8 G. Nocton, **P. Horeglad**, J. Pécaut, M. Mazzanti “Polynuclear Cation-Cation Complexes of Pentavalent Uranyl: Relating Stability and Magnetic Properties to Structure”

J. Am. Chem. Soc. **2008**, 130, 16633–16645; IF₂₀₀₈ = 8.091, IF₂₀₁₅ = 13.038, number of citations – 96⁶

- A9 **P. Horeglad**, G. Nocton, Y. Filinchuk, J. Pécaut, M. Mazzanti “Pentavalent Uranyl Stabilized by a Dianionic Bulky Tetradentate Ligand”

Chem. Commun. **2009**, 1843–1845; IF₂₀₀₉ = 5.504, IF₂₀₁₅ = 6.567, number of citations – 33⁶

- A10 V. Mougél, **P. Horeglad**, G. Nocton, J. Pécaut, M. Mazzanti “Cation-Cation Interactions: an Unforeseen Route to Stable Pentavalent Uranyl and to the Selective Assembly of Polymetallic Mixed-Valent Uranyl Complexes”

Angew. Chem. Int. Ed. **2009**, 48, 8477–8480; IF₂₀₀₉ = 11.829, IF₂₀₁₅ = 11.709, number of citations – 70⁶

- A11 G. Nocton, **P. Horeglad**, V. Vetere, J. Pécaut, L. Dubois, P. Maldivi, N. M. Edelstein, M. Mazzanti “Synthesis, Structure and Bonding of Stable Complexes of Pentavalent Uranyl”

J. Am. Chem. Soc. **2010**, 132, 495–508; IF₂₀₁₀ = 9.023, IF₂₀₁₅ = 13.038, number of citations – 83⁶

- A12 C. Camp, V. Mougél, **P. Horeglad**, J. Pécaut, M. Mazzanti “Multielectron Redox Reactions Involving C-C Coupling and Cleavage in Uranium Schiff Base Complexes”

- J. Am. Chem. Soc.* **2010**, *132*, 17374–17377; IF₂₀₁₀ = 9.023, IF₂₀₁₅ = 13.038, number of citations – 26⁶
- A13 V. Mougel, **P. Horeglad**, G. Nocton, J. Pécaut, M. Mazzanti “Cation-Cation Complexes of Pentavalent Uranyl: From Disproportionation Intermediates to Stable Clusters”
Chem. Eur. J. **2010**, *16*, 14365–14377; IF₂₀₁₀ = 5.476, IF₂₀₁₅ = 5.771, number of citations – 32⁶
- A14 **P. Horeglad***, P. Kruk, J. Pécaut "*Heteroselective Polymerization of rac-Lactide in the Presence of Dialkylgallium Alkoxides: The Effect of Lewis Base on Polymerization Stereoselectivity*"
Organometallics **2010**, *29*, 3729–3734; IF₂₀₁₀ = 3.888, IF₂₀₁₅ = 4.186, number of citations – 39⁶
- A15 **P. Horeglad***, G. Szczepaniak, M. Dranka, J. Zachara „*The first facile stereoselectivity switch in the polymerization of rac-lactide - from heteroselective to isoselective dialkylgallium alkoxides with the help of N-heterocyclic carbenes*”
Chem. Commun. **2012**, *48*, 1171–1173; IF₂₀₁₂ = 6.378, IF₂₀₁₅ = 6.567, number of citations – 48⁶
- A16 **P. Horeglad***, A. Litwińska, G. Z. Żukowska, D. Kubicki, G. Szczepaniak, M. Dranka, J. Zachara „*The influence of organosuperbases on the structure and activity of dialkylgallium alkoxides in the polymerization of rac-lactide: The road to stereo diblock PLA copolymers*”
Appl. Organometal. Chem. **2013**, *27*, 328–336; IF₂₀₁₃ = 2.017, IF₂₀₁₅ = 2.452, number of citations – 11⁶
- A17 E. Jabłonka-Gronowska, B. Witkowski, **P. Horeglad**, T. Gierczak, K. Grela „Testing the 1,1,3,3-tetramethyldisiloxane linker in olefin metathesis”
Compt. Rend. Chem. **2013**, *16*, 566–572; IF₂₀₁₃ = 1.483, IF₂₀₁₅ = 1.798, number of citations – 2⁶
- A18 **P. Horeglad***, O. Ablialimov, G. Szczepaniak, A. M. Dąbrowska, M. Dranka, J. Zachara „*Dialkylgallium complexes with alkoxide and aryloxy ligands possessing N-heterocyclic carbene functionalities: Synthesis and structure*”
Organometallics **2014**, *33*, 100–111; IF₂₀₁₄ = 4.126, IF₂₀₁₅ = 4.186, number of citations - 10⁶
- A19 E. Olędzka, **P. Horeglad**, Z. Gruszczyńska, A. Plichta, G. Nałęcz-Jawecki, M. Sobczak „Poly lactide conjugates of camptothecin with different drug release abilities”
Molecules **2014**, *19*, 19460–19470; IF₂₀₁₄ = 2.416, IF₂₀₁₅ = 2.465, number of citations – 6⁶
- A20 **P. Horeglad***, M. Cybularczyk, B. Trzaskowski, G. Z. Żukowska, M. Dranka, J. Zachara „*Dialkylgallium Alkoxides Stabilized with N-Heterocyclic Carbenes:*

Opportunities and Limitations for the Controlled and Stereoselective Polymerization of rac-Lactide

***Organometallics* 2015, 34, 3480–3496; IF₂₀₁₅ = 4.186, number of citations – 14⁶**

- A21 **P. Horeglad***, M. Cybularczyk, A. Litwińska, A. M. Dąbrowska, M. Dranka, G. (H6) **Z. Żukowska**, M. Urbańczyk, M. Michalak „*Controlling the stereoselectivity of rac-LA polymerization by chiral recognition induced the formation of homochiral dimeric metal alkoxides*”

***Polym. Chem.* 2016, 7, 2022–2036; IF₂₀₁₅ = 5.687, number of citations – 3⁶**

- A22 M. Cybularczyk, M. Dranka, J. Zachara, **P. Horeglad*** „The effect of In–C_{NHC} bond on the synthesis, structure and reactivity of dialkylindium alkoxides - how indium compares to gallium”

***Organometallics* 2016, 35, 3311–3322; IF₂₀₁₅ = 4.186**

Patent applications

- P1 **P. Horeglad**, G. Szczepaniak (10/P27647PL00; P.395130; 06.06.2011) „*New gallium complexes, their synthesis and application in the ring-opening polymerization of heterocyclic monomers.*” Polish patent granted to the Faculty of Chemistry University of Warsaw on the basis of the decision issued at 23.12.2013, The patent has not been paid.
- P2. **P. Horeglad**, M. Cybularczyk (10P38641PL00; 23.01.2017) „*Dialkylgallium and dialkylindium complexes and their application for the synthesis of PLA-drug conjugates and for the immortal ring-opening polymerization of heterocyclic monomers*” patent application.

Presentations at conferences

The works are presented in chronological order and refer only to the communicates presented in person. The works that are related to the cycle of publications which constitute the Work in accordance with the Act are shown in bold.

Before earning a Ph. D. degree

- K1 **P. Horeglad**, J. Lewiński, J. Zachara *Organometallic compounds of Al and Zn derived from maltol (3-hydroxy-2-methyl-4-pyrone)* Vth Regional Seminar of PhD-Students on Organometallic and Organophosphorous Chemistry, 1999, Seč-Pardubice, Czech Republic, oral presentation.
- K2 **P. Horeglad**, J. Lewiński, W. Grzenda, E. Lewińska, J. Lipkowski, E. Kołodziejczyk *The nature of active species in the ring-opening polymerization of lactones* VIIth Regional seminar of Ph.D-students on organometallic and coordination chemistry, 2002, Bad Kösen, Germany, oral presentation.
- K3 **P. Horeglad**, E. Tratkiewicz, J. Lewiński, Z. Ochal, J. Zachara, I. Justyniak, J. Lipkowski *Towards the nature of ring-opening transformations of epoxides* XXIIIrd

- Poland-Germany Colloquy on Organometallic Chemistry, 2003, Wierzba, Poland, poster.
- K4 **P. Horeglad**, E. Tratkiewicz, J. Lewiński, Z. Ochal, J. Zachara, J. Lipkowski, I. Justyniak *The nature of AlMe₃ mediated ring-opening transformations of 2,3-epoxy-1-alkanols* Organo Metallic Chemistry directed towards Organic Synthesis, 2003, Toronto, Canada, poster.
- K5 **P. Horeglad**, J. Lewiński, E. Tratkiewicz, J. Lipkowski, E. Kołodziejczyk *Nature of Active Sites in the Polymerization of ε-Caprolactone and Propylene Oxide* VIIIth Seminar of PhD Students on Organometallic Chemistry, 2003, Hrubá Skála, Czech Republic, oral presentation.
- K6 J. Lewiński, **P. Horeglad**, E. Tratkiewicz, K. Suwała, I. Justyniak, J. Lipkowski, E. Kołodziejczyk *Effect of structure of aluminium active sites on the polymerization activity towards lactones and lactides* III Polish-Ukrainian Conference „Polymers of special applications”, 2004, Radom, Poland, poster.
- K7 **P. Horeglad**, J. Lewiński, I. Justyniak *On the role of chelation effect and coordination number in the ring-opening polymerization initiated by aluminum alkoxides* 5th International School on Molecular Catalysis, 2005, Poznań-Rosnówko, Poland, poster.
- K8 **P. Horeglad**, J. Lewiński, I. Justyniak. *Chelation effect and coordination number – parameters influencing ring-opening polymerization of aluminum alkoxides* XVI FEICHEM Conference on Organometallic Chemistry, 2005, Budapest, Hungary, poster.

After earning a Ph. D. degree

- K9 **P. Horeglad**, M. Schürmann, J. Lewiński, K. Jurkschat *The competition between P=O···X (X = I, Br) interaction and P=O···H hydrogen bond in iodine and bromine compounds containing an O,C,O- coordinating pincer-type ligand* XVIII International Conference on Physical Organic Chemistry, 2006, Warsaw, Poland, poster.
- K10 **P. Horeglad**, J. Lewiński, I. Justyniak *On the role of chelation effect and coordination number in ring-opening of cyclic esters initiated by aluminum alkoxides* Xth International Seminar of Ph.D Students on Organometallic and Coordination Chemistry, 2006, Medlov, Czech Republic, invited lecture.
- K11 **P. Horeglad**, G. Nocton, F. Burdet, J. Pécaut, M. Mazzanti *How to stabilize UO₂⁺ species* XXIII International Conference on Organometallic Chemistry, 2008, Rennes, France, poster.
- K12 **P. Horeglad**, G. Nocton, J. Pécaut, M. Mazzanti *Stability and reactivity of pentavalent uranyl complexes* 39èmes Journées des Actinides, 2009, La Grande Motte, France, oral presentation.
- K13 **P. Horeglad** *Gallium alkoxides – new promising initiators for the well controlled and stereoselective polymerization of lactide?* 17th International Symposium on Homogeneous Catalysis, 2010, Poznań, Poland, poster.
- K14 **P. Horeglad**, G. Szczepaniak, M. Dranka, J. Zachara *The first facile switch between heteroselective and isoselective gallium alkoxides in the polymerization of rac-lactide* XIX EuCheMS Conference on Organometallic Chemistry, 2011, Toulouse, France, poster.

- K15 P. Horeglad *Coordination polymerization – from polyolefines to biodegradable polymers (in Polish)* XXXVI Ogólnopolska Szkoła Chemii (XXXVI Polish School of Chemistry), 2012, Rynia, Poland, invited lecture.
- K16 P. Horeglad *Gallium alkoxides – new catalysts offering facile stereoselectivity switch in the polymerization of racemic lactide* XXV International Conference on Organometallic Chemistry, 2012, Lisbon, Portugal, oral presentation.
- K17 P. Horeglad *Alkoxygallium complexes – new catalysts allowing for the inversion of stereoselectivity in the polymerization of racemic lactide (in Polish)* 55 Zjazd PTChem i SiTPChem (55th Polish Chemical Society Meeting), 2012, Białystok, Poland, oral presentation.
- K18 P. Horeglad *The effect of N-heterocyclic carbenes on the structure and properties of dialkylgallium alkoxides (in Polish)* 57 Zjazd Naukowy PTChem i SiTPChem (57th Polish Chemical Society Meeting), 2014, Częstochowa, Poland, oral presentation.
- K19 P. Horeglad *Dialkylgallium and indium alkoxides and aryloxides with N-heterocyclic carbenes - from fundamental aspects of M–C_{NHC} bond to stereoselective catalysts for the polymerization of rac-lactide* 21st Conference on Organometallic Chemistry (EuCOMC XXI) 2015, Bratislava, Slovakia, oral presentation.
- K20 P. Horeglad *Heteroselective polymerization of rac-lactide in the presence of dialkylgallium alkoxides – do we face a new mechanism of stereocontrol? (in Polish)* 58 Zjazd Naukowy Polskiego Towarzystwa Chemicznego (58th Polish Chemical Society Meeting), 2015, Gdańsk, Poland, oral presentation.
- K21 P. Horeglad *Dialkylgallium alkoxides - catalysts for the controlled and stereoselective polymerization of rac-LA* POLYMAT 2016 - Silesian Meetings on Polymer Materials, 2016, Zabrze, Poland, poster.
- K22 P. Horeglad *How to switch stereoselectivity in the polymerization of rac-LA - a curious case of dialkylgallium and dialkylindium alkoxides* 42nd International Conference on Coordination Chemistry, Brest, France, oral presentation.

The works presented, by students working under my supervision, at international conferences.

The names of presenting persons are underlined.

- K23 A. Litwińska, G. Z. Żukowska, D. Kubicki, P. Horeglad *The effect of tertiary amines on the structure, activity and stereoselectivity of dialkylgallium alkoxides in the polymerization of rac-lactide* Międzynarodowy Kongres Młodych Chemików YoungChem, 2012, Gdańsk, Poland, poster.
- K24 A. M. Dąbrowska, M. Dranka, J. Zachara, P. Horeglad *Dialkylgallium complexes with alkoxide and aryloxy ligands possessing N-heterocyclic carbene functionalities* Frühjahrsymposium – spring symposium, 2014, Jena, Germany, poster.
- K25 A. M. Dąbrowska, P. Horeglad *Dialkylgallium complexes with alkoxide and aryloxy ligands possessing N-heterocyclic carbene functionalities* XV International Seminar of PhD Students on Organometallic and Coordination Chemistry, 2014, Świeradów Zdrój, Poland, oral presentation.
- K26 M. Cybularczyk, P. Horeglad *The reactivity of dialkylindium alkoxides towards N-*

heterocyclic carbenes (NHC) – How does indium compare to gallium? XV International Seminar of PhD Students on Organometallic and Coordination Chemistry, 2014, Świeradów Zdrój, Poland, oral presentation.

- K27 A. M. Dąbrowska, **P. Horeglad** *Dialkylgalliumj aryloxide complexes with N-heterocyclic carbenes. Synthesis, structure, properties* Frühjahrsymposium – spring symposium, 2015, Münster, Germany, poster.
- K28 M. Cybularczyk, **P. Horeglad** *The influence of structure of dialkylindium alkoxides and aryloxides on its reactivity towards N-heterocyclic carbenes (NHC)* 10th International School of Organometallic Chemistry, 2015, Camerino, Italy, poster.
- K28 M. Cybularczyk, A. Litwińska, A. M. Dąbrowska, **P. Horeglad** *Chiral recognition – a new tool to control the stereoselectivity of metal alkoxides in the ring-opening polymerization of rac-LA* POLYMAT 2016 - Silesian Meetings on Polymer Materials, 2016, Zabrze, Poland poster.

Principal Investigator (and main investigator) of research grants

Before earning of a Ph. D. degree

1. Komitet Badań Naukowych (National Comitee of Scientific Research) - grant promotorski nr 3 T09B 097 26 (grant for Ph. D. students, called „supervisor’s grant”), *The synthesis of biodegradable polymers with alkoxyaluminum catalysts*, from 01/2004 to 06/2005, Faculty of Chemistry, Warsaw University of Technology – **main investigator**.

After earning of a Ph. D. degree

1. Ministry of Science and Higher Education of Poland - IUVENTUS PLUS grant (IP2010012970) *Gallium alkoxide complexes – new catalysts for the controlled and stereoselective polymerization of cyclic esters*, from 12/2010 to 12/2011, Faculty of Chemistry, University of Warsaw – **principal investigator**.
2. National Science Center of Poland - grant SONATA BIS 2 (DEC-2012/07/E/ST5/02860) *The effect of strong Lewis bases on the structure of group 13 and 14 metal alkoxides and their catalytic activity in the polymerization of heterocyclic monomers*, from 09/2013 to 09/2018, Centre of New Technologies, University of Warsaw – **principal investigator**.
3. Foundation for Polish Science – IMPULS competition within SKILLS project (150/UD/SKILLS/2015) *Direct synthesis of polylactide – β -blocker conjugates with the use of dialkylgallium alkoxides*, from 08/2015 to 10/2016, Centre of New Technologies, University of Warsaw – **principal investigator**.

Scientific trainings

Before earning a Ph. D. degree

09/2004 - Short term training in the research group of Prof. Klaus Jurkschat (University
11/2004 of Dortmund, Dortmund, Germany) – synthesis and characterization of
bromine, iodine and zinc derivatives of O,C,O pincer type ligand.

After earning a Ph. D. degree

05/2007 - Post doctoral training in the research group of Dr. Marinella Mazzanti
05/2009 (Commissariat à l'Energie Atomique, Grenoble, France) – synthesis, structure
and reactivity of uranyl complexes at +5 oxidation state.

Scientific collaboration

1. Since 2010 I have been collaborating with Dr. Maciej Dranka and Prof. Janusz Zachara from Faculty of Chemistry, Warsaw University of Technology concerning the characterization of investigated complexes with the use of X-ray analysis as well as the use of Bond Valence Vector Model in the research on the structure of investigated complexes.
2. Since 2012 I have been collaborating with Prof. Ewa Olędzka and Prof. Marcin Sobczak from Medical University of Warsaw concerning the synthesis of PLA-drug conjugates with the use of PLA matrices of defined microstructure.
3. Since 2016 I have been collaborating with Dr. Andrzej Plichta from Faculty of Chemistry, Warsaw University of Technology concerning the use of dialkylgallium alkoxides for the synthesis of PLA and PLA copolymers.

Overall scientific input from 2001 to 2017

publications listed at the Journal

Citation Reports (JCR) database:	21 (in 7 of them I am the corresponding author)
summary IF:	101.773 (publication year) 123.860 (2015)
citations without self citations:	587 (WoS), 628 (Scopus)
citations (sum):	641 (WoS), 681 (Scopus)
Hirsch index:	13 (WoS), 14 (Scopus)
Hirsch index (without self citations):	12 (WoS), 12 (Scopus)

Before earning a Ph. D. degree

publications listed at the Journal

Citation Reports (JCR) database: **6** (A1, A3-A7)
summary IF: **18.460** (publication year) **24.986** (2015)
conference contributions: **8** (domestic and international)

After earning a Ph. D. degree (in 2006)

publications listed at the Journal

Citation Reports (JCR) database: **15** (A8-A22)

Out of 15 publications, 6 constitute the series of thematically related scientific papers (**H1-H6**), which is an achievement under Art. 16 paragraph. 2 of the Act of 14th of March 2003 on academic degrees and academic titles and degrees and title in art (Dz. U. No. 65, item. 595, as amended.) In all of them I am the corresponding author.

summary IF: **83.313** (publication year) **98.874** (2015)
conference contributions: **14** (domestic and international)
invited lectures: **2**

5. Teaching activities

Classes for students

In the course of my work at the Faculty of Chemistry, Warsaw University of Technology I ran the following classes for students:

1. Laboratory classes – the basics of chemical technology: „Catalysis with metal complexes” in 2001 - 2004 and 2006 – 2007 (IIIrd year of M. Sc. Studies)
2. Laboratory of technological design, in 2002 (IVrd year of M. Sc. Studies)
3. Laboratory of advanced inorganic chemistry: „Activation of molecular oxygen with organometallic complexes”, in 2006 – 2007 (IIIrd year of M. Sc. Studies).

In the course of my work at the Faculty of Chemistry, University of Warsaw, I ran the Individual Additional Laboratory classes (optional classes for students (45 hours) according to my own program) in 2010/2011.

Supervising B. Sc. and M. Sc. students

In the course of my work at the Faculty of Chemistry, Warsaw University of Technology I co-supervised 3 M. Sc. students (Anna Grzegdała – 2003 r., Anna Rola – 2005 r., Katarzyna Wójcik 2006 r.).

In the course of my work at the Faculty of Chemistry and Centre of New Technologies, University of Warsaw, I supervised 3 B. Sc. students (Anna Maria Dąbrowska – 2013, Ewa

Pindara – 2013, Rafał Zaremba – 2016) and 2 M. Sc. students (Anna Litwińska – 2012, Anna Maria Dąbrowska – 2015). My students took part in the research work and are co-authors of articles **A16 (H3)**, **A18 (H4)** and **A21 (H6)** and several conference presentations.

Currently, under my supervision, Rafał Zaremba – M. Sc. student conducts the research work of SONTA BIS grant.

Supervising Ph. D. students

In the course of my work at the Centre of New Technologies, University of Warsaw

I have been called as a co-supervisor of Ph. D. student – Martyny Cybularczyk, M. Sc. by the Faculty of Chemistry, University of Warsaw. Martyna Cybularczyk, M. Sc. conducts the research within my SONTA BIS grant and is a co-author of publications **A20 (H5)**, **A21 (H6)** and **A22**.

I also supervise the research work of Aleksander Hurko, M. Sc. who works within my SONATA BIS grant on germanium complexes stabilized with N-heterocyclic carbenes.

Invited Lectures

I have delivered 3 invited lectures, including the lecture **K15** at XXXVI Ogólnopolskiej Szkoły Chemii (Polish School of Chemistry). The two remaining include:

1. „*Quo vadis chemicus? How to choose good scientific problem and survive*” invited by the students of Chemical Scientific Society "Fulleren" of the Faculty of Chemistry, University of Warsaw (10.06.2014)
2. „*Acting on purpose or accidentally? How we synthesized switchable catalysts*” invited by the students of Chemical Scientific Society "Flogiston" of the Faculty of Chemistry, Warsaw University of Technology (10.06.2015)

Laboratory classes for secondary school students

With my research team (Organometallic Chemistry Laboratory at Centre of New Technologies, University of Warsaw) we have already hosted students from secondary schools twice. In the cooperation with National Found for Children we organized a four day workshop „*How to build a polymer- how the catalyst works*” in June 2015 and 2016.

6. Organizational activities

Membership and activities in professional associations

Since 2013 Member of the Board of the Warsaw Branch of the Polish Chemical Society

Activity as a reviewer

Reviews for scientific journals worldwide

No of reviews	journal, <i>publisher</i>
23	Synthetic Metals, <i>Elsevier</i>
4	Inorganic Chemistry, <i>American Chemical Society</i>
3	Catalysis Communications, <i>Elsevier</i>
3	European Journal of Inorganic Chemistry, <i>Wiley</i>
1	ACS Catalysis, <i>American Chemical Society</i>
1	Macromolecules, <i>American Chemical Society</i>
1	Organometallics, <i>American Chemical Society</i>
1	Catalysis, Science&Technology, <i>Royal Society of Chemistry</i>
1	Dalton Transactions, <i>Royal Society of Chemistry</i>
1	Polyhedron, <i>Elsevier</i>
1	Chemical Monthly, <i>Springer</i>

The sum 40

Reviews of grant applications

I was a member of the team of experts, of the National Science Centre of Poland, reviewing grant applications, in 2015.

Conference organization

2015	member of the organizing comitee of ChemSession'15, XII th Warsaw Seminar of PhD students in Chemistry, Warsaw
2016	Member of the scientific comitee of of ChemSession'16, XIII th Warsaw Seminar of PhD students in Chemistry, Warsaw

Paweł Horeglad



Warsaw, 22.02.2017 r.