Annex No. 3

Auto-presentation in English

1. **Name and surname:** Agnieszka Bukowska

2. Diplomas and degrees

1988	Master of Science. Engineer Area/specialization: chemistry/ chemistry and organic technology Rzeszów University of Technology, Faculty of Chemistry Master's thesis: Polyfunctional autocatalytic and coupled reactions Supervisor: Edward Rokaszewski, PhD, Eng.
1991	Doctor of chemical sciences Area/discipline: chemical sciences/ chemical kinetics and catalysis Dmitry Mendeleev University of Chemical Technology of Russia PhD thesis: „Kinetics and mechanism of reactions of terminal epoxides with carboxylic acids" Supervizor: prof. V. F. Shvets Reviewers: prof. G.K. Shestakov, M.V. Lomonosov Moscow State University of Fine Chemical Technologies doc. V.G. Sharykin, The State Research and Design Institute of Paint and Varnish Industry, Moscow

3. INFORMATION ON EMPLOYMENT IN SCIENTIFIC UNITS

07.1988 – 01.1992	Assistant Rzeszów University of Technology, Faculty of Chemistry,
1992 – present	Assistant professor Rzeszów University of Technology, Faculty of Chemistry,

4. Presentation of scientific achievements resulting from Art. 16 clause 2 of the Act dated 14 March 2003 on scientific degrees and scientific titles and degrees and titles in arts (Dz.U. of 2003, no. 65, item 595, as amended)

a) author/authors, title/titles of publications, year of publishing, name of publisher:

Title of scientific achievements

I herein indicate a series of 16 publications (12 listed in the database of Journal Citation Reports, JRC) and 1 patent as a scientific achievement entitled:

"POLYMER GELS FOR SORPTIVE AND CATALYTIC PURPOSES"

and constituting a basis for the application for the award of scientific degree of doctor of science (habilitation) in the area of chemistry.

Related to the subject of the relevant achievement as well, another series of eight articles resulted from the collaboration with teams supervised by prof. A. Drelinkiewicz from Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences as well as prof. J. Ziółkowski and prof. A. Trzeciak from the Faculty of Chemistry, at University of Wrocław, for which I synthesized and characterized polymer supports for palladium catalysts for the reactions of hydrogenation of 2-butyne-1,4-diol and maleinic and fumaric acids (JHICSCh PAS), and Suzuki-Miyaura coupling (FCh UW).

List of studies constituting a single-topic series of publications related to the scientific achievement, arranged by the year of publication, *with percentage contribution of the habilitant to each work*

Impact Factor (IF) – value for the year of publication

H1	**Bukowska A.**, Bukowski W., Noworól J., New 2-Hydroxyethyl Methacrylate Resins with Good Swelling Characteristics, *J. Appl. Polym. Sci.*, 2006, 101, 1487-1493. **IF – 1.306**, I contributed to this publication by developing a methodology for synthesis and characterization of hydroxyl functionalized swellable gels, performing a part of analysis and measurements, including DSC measurements, and by co-writing the manuscript of this paper. Contribution - 40%.
H2	Bukowski W., **Bukowska A.**, Noworól J., Myśliwiec B., Wbudowanie chelatujacego układu iminowego w terpolimery metakrylanu glicydylu, *Polimery* (Warsaw), 2006, 51(11-12), 787- 793. **IF – 1.137,** I designed the concept for using epoxy functionalized polymer for preparation of reactive sorbents for transition metal ions. I contributed to this publication by developing a methodology for chemical modification of epoxy functionalized polymer gels towards obtaining the reactive polymers with amine-imine chelating units, the methodology for characterization of the gels, and co-writing the manuscript of this paper. Contribution - 45%.
H3	**Bukowska A.**, Bukowski W., Glycidyl Methacrylate Copolymers Modified of Diamines as Effective Nucleophilic Scavengers, *Polish J. Chem. Technol.*, 2006, 8(3), 73-75, I designed the concept for using epoxy functionalized polymer in preparation of nucleophilic scavenging resins. I contributed to this publication by developing a methodology for chemical modification of epoxy functionalized polymer gels towards obtaining reactive polymers with polyamine functions, by developing methodology for characterization of the synthesized polymers, performing all the experiments of chemical modification of glycidyl methacrylate polymers, and tests examining their application as scavenging resins, and by co-writing the manuscript of this paper.

	Contribution - 70%.
H4	**Bukowska A.**, Bukowski W., Noworól J., Three-Component Terpolymers of Glycidyl Methacrylate Microbeads with Good Swelling Characteristics, *J. Appl. Polym. Sci.*, 2007, 106, 3800-3807. **IF – 1.008,** I contributed to this publication by developing a methodology for synthesis of glycidyl methacrylate swellable gels and their characterization, by performing a part of polymerization experiments and analyses, including DSC measurements, and co-writing the manuscript of this paper. Contribution - 40%.
H5	**Bukowska A.**, Bukowski W., Synthesis Co(salen) Complexes Immobilized onto the HEMA-Resin and their Catalytic Activity in the Reaction of Epoxides with Carboxylic acids, *React. Funct. Polym.*, 2008, 68, 657-670. **IF – 2.039,** I contributed to this publication by planning and performing the synthetic and catalytic experiments and co-writing the manuscript of this paper. Contribution - 50%.
H6	**Bukowska A.**, Bukowski W., Noworól J., Catalytic Activity of Schiff Base Cobalt(III) Complexes Immobilized on Terpolymers of Glycidyl Methacrylate in the Addition of Carboxylic Acids to Terminal Epoxides, *J. Appl. Polym. Sci.*, 2010, 117, 655–663. **IF – 1.24,** I contributed to this publication by developing a methodology for synthesis of polymer supported cobalt catalysts and their characterization, by performing a part of the synthetic and catalytic experiments, and co-writing the manuscript of this paper. Contribution - 45%.
H7	**Bukowska A.,** Bukowski W., Machowski D., Chemosorpcja aldehydów na żelach metakrylanowo-styrenowych z pierwszorzędowymi funkcjami aminowymi, *Polimery*, 2010, 55 (7-8), 29-38, I developed the concept for using the modified resins with amine units as materials capturing electrophilic contaminants from reaction mixtures. I contributed to this publication by developing a methodology for sorptive experiments, performing all the synthetic experiments and a part of sorptive experiments, and co-writing the manuscript of the paper. I was the main author of the study. Contribution - 70%.
H8	Matkiewicz K., **Bukowska A.**, Bukowski W., Hydroxyl Functionalized Methacrylic Terpolymers as Supports for Mn(III)Salen Catalysts and Their Application in Asymmetric Epoxidation, *J. Inorg. Organometal. Polym. Mat.*, 2012, 22, 332-341. **IF – 1.174,** I contributed to this publication by developing the procedures of synthesis and characterization of polymer supported chiral salen Mn(III) complexes and their utylization in epoxidation reactions, performing a part of synthetic and analytical experiments, and co-writing the manuscript of this paper. Contribution - 40%.
H9	**Bukowska A.**, Bukowski W., Polyamine Functionalized Glycidyl Methacrylate Terpolymers as Scavengers for Metal Ions Uptake from Organic Solutions, *J. Appl. Polym. Sci.*, 2012, 124(2), 904-912. **IF – 1.395,** I designed the concept for the use of the resins with polyamine units for metal ion uptake from organic solutions. I contributed to this publication by developing a methodology for synthetic and sorptive experiments, performing all the synthetic and sorptive experiments, and co-writing the manuscript of this paper. I was the main author of the study. Contribution - 70%.
H10	Bester K., **Bukowska A.**, Bukowski W., Synthesis of Gel-type Imino-Amino Functionalized Methacrylate-Styrene Terpolymers as Supports for Palladium Catalysts for the Suzuki-Miyaura Reaction, *Appl. Catal. A: General*, 2012, 443-444,181-190. **IF – 3.41,** I contributed to this publication by developing the procedures for synthesis of polymer supported palladium catalysts with amine-imine units and methodology for their characterization and catalytic testing, including chromatographic analysis, by performing a part of synthetic and catalytic experiments and analyses, and co-writing the manuscript of this paper.

	Contribution - 45%.
H11	Matkiewicz K., **Bukowska A.**, Bukowski W., Novel Highly Active Polymer Supported Chiral Co(III)-Salen Catalysts for Hydrolytic Kinetic Resolution of Epichlorohydrin, J. *Mol. Catal. A-Chem.*, 2013, 368–369, 43–52. **IF – 3.679,** I contributed to this publication by developing the procedures for synthesis of polymer supported salen cobalt(III) complexes and a methodology for catalytic studies, including chromatographic analysis, by performing a part of synthetic and catalytic experiments and analyses; and co-writing the manuscript of this paper. Contribution - 40%.
H12	Bester K., **Bukowska A.**, Bukowski W., Palladium Catalysts Supported on Amine-Functionalized Glycidyl Methacrylate Gel-Type Terpolymers. Synthesis, Characteristics and Study of Catalytic Activity in Suzuki-Miyaura Reactions, *J. Mol. Catal. A-Chem.*, 2013, 378, 124-134. **IF – 3.679,** I contributed to this publication by developing the procedures for synthesis of polymer supported palladium catalysts with amine units and a methodology for their characterization and catalytic testing, including chromatographic analysis, by performing a part of synthetic and catalytic experiments and analyses; and co-writing the manuscript of this paper. Contribution - 45%.
H13	**Bukowska A.**, Bukowski W., Bester K., Flaga S., Linkage of the PAMAM type dendrimer with the gel type resin based on glycidyl methacrylate terpolymer as a method of preparation of the polymer support for the recyclable palladium catalyst for Suzuki–Miyaura cross-coupling reactions, *RSC Adv.*, 2015, 5, 49036-49044. **IF – 3.84,** I designed the concept for and was the main author of the study. I developed the methodology for synthesis of resins with dendritic system and their utilization in preparing polymer supported catalysts. I contributed to this publication by performing most synthetic and catalytic experiments and a part of analyses, and co-writing the manuscript of this paper. Contribution - 60%.
H14	**Bukowska A**., Bukowski W., Pytel M.: Scavenging Properties of the Polyamine Functionalized Gels Based on the Glycidyl Methacrylate Terpolymers, *Open J. Polym. Chem*., 2015, 5, 63-73. I designed the concept for the study. I contributed to this publication by performing all the synthetic and sorption experiments, and co-writing the manuscript of the paper. Contribution - 70%.
H15	**Bukowska A.**, Bukowski W., Kleczyńska S., Dychtoń K., Drajewicz M., Hydroxy functionalized porous polymer particles derived from mixtures of hydrophilic and hydrophobic monomers, *Polimery,* 2016, 9, 10-18. **IF – 0.633,** I proposed the concept for the use of the modified suspension polymerization technique for synthesis of new porous polymer materials. I coordinated the performance of the experimental part. I was the corresponding author for this publication. Contribution - 50%.
H16	**Bukowska A.**, Bukowski W., Kleczyńska S., Matkiewicz K., Hydrolytic kinetic resolution of racemic glycidyl esters on a polymer supported chiral salen cobalt(III) complex, *Chemik*, 2016, 70, 262-265. I proposed the concept for the study and I coordinated the performance of the experimental part. I was the corresponding author for this publication. Contribution - 45%.

Total IF – 24.537

H17	Bester K., **Bukowska A.**, Bukowski W., 2015, Heterogeniczny prekatalizator palladowy dla reakcji krzyżowego sprzęgania i sposób jego wytwarzania, Patent PL 222508, Polish Patent Office.

	I contributed significantly to the concept for the use of the carboxyl functionalized resins for preparation of the polymer supported palladium catalysts for cross-coupling reactions. Contribution - 55%.

Declarations of the co-authors regarding their contributions to joint publications are included in Annex 4. Full texts of the articles are included in Annex 6.

4.1. List of additional publications related to the subject of the scientific accomplishment

HD1	Knapik A., Drelinkiewicz A., Waksmundzka-Góra A., **Bukowska A.**, Bukowski W., Noworól J., Hydrogenation of 2-butyn-1,4-diol in the Presence of Functional Crosslinked Resin Supported Pd Catalyst. The Role of Polymer Properties in Activity/Selectivity Pattern, *Catal. Lett.* 2008, 122, 155-166. IF – 1.867.
HD2	Knapik A., Drelinkiewicz A., Szaleniec M., Makowski W., Waksmundzka-Góra A., **Bukowska A**., Bukowski W., Noworól J., Hydrogenation of Unsaturated Carboxylic Acids on Functional Gel-type Resin Supported Pd Catalysts: The Effect of Reactant Structure, *J. Mol. Catal. A: Chemical*, 2008, 279**,** 47–56. IF – 2.814.
HD3	Drelinkiewicz A., Knapik A., Waksmundzka-Góra A., **Bukowska A.**, Bukowski W., Noworól J., Functional Gel-type Resin Based Palladium Catalysts: The Role of Polymer Properties in the Hydrogenation of the C=C Bond of Maleic and Fumaric Acids, the Isomers of Dicarboxylic Acids, *React. Funct. Polym.*, 2008, 68, 1059-1071. IF – 2.029.
HD4	Drelinkiewicz A., Knapik A., Stanuch W., Sobczak J., **Bukowska A.**, Bukowski W., Diamine Functionalized Gel-type Resin as a Support for Palladium Catalysts: Preparation, Characterization and Catalytic Properties in Hydrogenation of Alkynes, *Reac. Funct. Polym*., 2008, 68, 1650–1662. IF – 2.039.
HD5	Drelinkiewicz A., Stanuch W., Knapik A., Ghanem A., Kosydar R., **Bukowska A.**, Bukowski W., Amine Groups Functionalized Gel-type Resin Supported Pd Catalysts: Physicochemical and Catalytic Properties in Hydrogenation of Alkynes, J. *Mol. Catal. A: Chemical*, 2009, 300, 8–18. IF – 3.135.
HD6	Duraczyńska D., Drelinkiewicz A., Serwicka E.M., Rutkowska-Zbik D., Bielańska E., Socha R., **Bukowska A.**, Bukowski W., Preparation and Characterization of $RuCl_3$ – Diamine Group Functionalized Polymer, *React. Funct. Polym*., 2010, 70, 382-391. IF – 2.546.
HD7	Trzeciak A.M., Mieczyńska E., Ziółkowski J.J., Bukowski W., **Bukowska A.**, Noworól J., Okal J., Palladium(0) Nanoparticles Encapsulated in Diamine-modified Glycidyl Methacrylate Polymer (GMA-CHDA) Applied as Catalyst of Suzuki-Miyaura Cross-coupling Reaction, *New J. Chem.*, 2008, **32**, 1124 – 1130. IF – 2.942.
HD8	Borkowski T., Trzeciak A.M., Bukowski W., **Bukowska A.**, Tylus W., Kępiński L., Palladium(0) Nanopareticles Formed in situ in the Suzuki-Miyaura Reaction: The Effect of a Palladium(II) Precursor, *Appl. Catal. A: General*, 2010, 378, 83-89. IF – 3.383.

I contributed to publications **HD1-HD8** by performing the syntheses and basic analysis of the polymer gels used as supports for palladium or ruthenium catalysts.
My estimated contribution – 5-10%.

b) Overview of the scientific purpose of the above studies and the findings, and discussion of their possible application

My scientific interests and research performed at the Faculty of Chemistry, at Rzeszów University of Technology for the last 10 years have focused mainly on synthesis and practical applications of reactive polymer gels. I have designed and synthesized a series of reactive gels which could be used for the fast removal of selected organic electrophiles (e.g. aldehydes, acid chlorides and isocyanates) and selected transition metal ions (e.g. Co(II), Cu(II), Mn(II), Ni(II), Fe(III), Pd(II)) from organic solutions, and I explored their use as supports for catalysts of reactions of epoxide ring opening (including the hydrolytic kinetic resolution of terminal racemic epoxides), asymmetric epoxidation, hydrogenation, C-C and C-N cross-coupling as well as A3 coupling. The research was financed partly by ministerial grant no. N205 015234 entitled "New polyfunctional polymer reagents for selective removal of selected molecules and metal complexes from post-reaction solutions" in which I was the principal researcher. Moreover, I have contributed to other subsidized research projects as a co-investigator; these include: "Synthesis of functionalized copolymers as potential supports for catalysts" (3 T09B 090 26), "Chiral cobalt(III) and manganese(III) complexes immobilized on methacrylate-styrenic terpolymers in selected catalytic applications" (N N204 131737) and "New catalytic materials as a base for environmental friendly chemical processes. Pd dispersed in polymer matrices – new catalytic systems for processes of unsaturated hydrocarbon hydrogenation" (K124/T09/2005), which enabled me to support financially a part of my experiments.

The career of reactive polymer materials in organic synthesis started in the early 1960s when Merriefield published his article on possible application of functionalized copolymers of styrene and divinylbenzene in peptide synthesis [1]. This work led to rapid development in synthesis of reactive polymeric materials and contributed to their more widespread applicability, initially, in peptide synthesis (*solid phase peptide synthesis*, *SPPS*), and then as a new method of organic synthesis known at present as *solid phase organic synthesis* (*SPOS*) [2-9]. Over time, further possibilities for applying reactive polymer materials in organic synthesis appeared, in particular, related to their use as supports for specific reagents and catalysts, or as sorbents for fast removal of reactive contaminants from reaction products (e.g. some side-products or excess reactants) [7-18].

Research findings proved that from the viewpoint of reactive polymer resins applicability for synthetic uses, their beads should not be smaller than 100 and larger than 400 mesh (the commercially available resins are generally sold as spherical beads with the size in the ranges of 100-200 or 200-400 mesh). In practice, the beads which are too small make it difficult to handle the resins. Furthermore, an increase in the bead size leads to unfavourable ratio of functional groups to the polymer surface, and to a decrease in their mechanical strength [19, 20].

The commercially available resins are commonly based on copolymers of styrene (S) and divinylbenzene (DVB), obtained using the suspension polymerization method, which are then chemically modified to obtain further functionalization [7, 9, 20-24]. An alternative method of synthesising reactive polymer gels involves the use the properly functionalized styrene derivatives at the stage of polymerization.

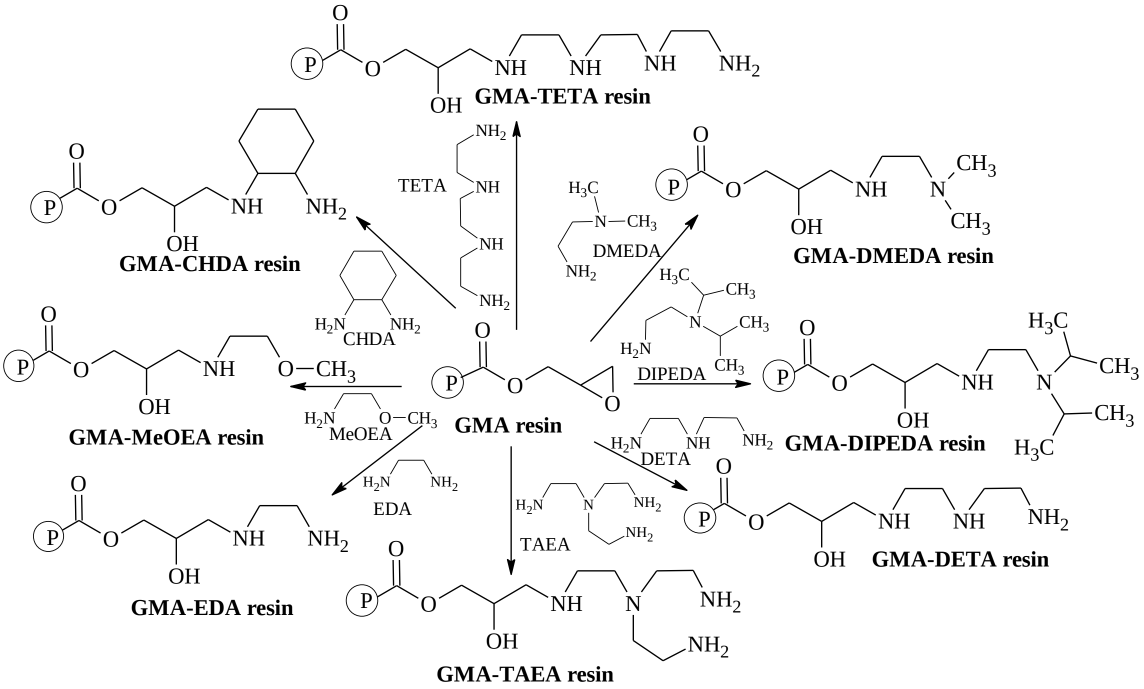
In order to create an alternative to the commercially available polymeric resins, we decided to use the easily available esters of methacrylic acid - glycidyl methacrylate (GMA) and 2-hydroxyethyl methacrylate (HEMA) (2-hydroxypropyl as well as 2-hydroxy-3-phenoxypropyl methacrylates as the functional monomers for synthesis of the new reactive gels. The monomers were subjected to suspension polymerization with styrene and various cross-linking monomers (e.g. divinylbenzene (DVB) or diethylene glycol dimethacrylate (DMGDE)). As a result, it was possible to obtain non-porous polymer gels with different cross-linking degree and functional group loadings (the loading of epoxy or hydroxyl groups in mmol per resin gram). By optimizing the monomer composition and the conditions of polymerization we obtained resins compatible with numerous polar and non-polar solvents, as well as thermally stable; they could be modified relatively easily to introduce new functionalities.

Prof. W. Bukowski proposed the use of functionalized methacrylates in synthesis of resins with reactive epoxy or hydroxyl groups (abbreviated hereinafter as **GMA** and **HEMA** gels, respectively). I was appointed with the task of developing the synthesis conditions and methodology for characterization of the obtained polymer beads. The study was funded by ministerial grant [25], and I was one of the main researchers in the project. The relevant findings were described in two articles published in *J. Appl. Polym Sci*,. **H1**, **H4**.

Good swelling ability of the **GMA** and **HEMA** gels in various organic solvents created favourable conditions for their further chemical modification towards the preparation of reactive polymer materials characterized by different functionality. The resulting products could successfully be utilized for sorptive and catalytic purposes. This issue became a leading topic of my further research.

While planning the work on the synthesis of polyfunctional polymer reagents I thoroughly reviewed the previous achievements in the field of preparation and use of scavenging resins. The information gathered on this occasion was used, on the one hand, to prepare a review article published in *Wiadomości Chemiczne* [26]; on the other hand, it inspired me to use the **GMA** resins for synthesis of polymer reagents with polyamine functions, which, as it was shown by further studies, could be used directly for purifying reaction products from undesired impurities, e.g. excess of electrophilic reactants, including acid chlorides, isocyanates, and aldehydes, and for sorption of transition metal ions.

Thus, utilizing the ability of epoxy groups in the **GMA** resins to react with amines, I synthesized a series of nucleophilic resins with ethylenediamine (EDA), diethylenetriamine (DETA) and tris-(2-aminoethyl)amine (TAEA)) functions. In course of further work, an analogous method was applied to synthesize resins with units of *trans*-1,2-diaminocyclohexane (CHDA), triethylenetetramine (TETA), N,N-dimethylethylenediamine (DMEDA), N,N-diizopropylethylenediamine (DIPEDA), 2-methoxyethylamine (MeOEA) (Scheme 1), which were then used for the preparation of palladium catalysts.



Scheme 1. Variants of chemical modification of the **GMA** resin to obtain a series of resins with (poly)amine functions.

While optimizing the conditions for the synthesis of the resins with polyamine units I explored the effects of an amine excess and a reaction medium in the course of modification in the GMA resins with varying degrees of functionalization and cross-linking. The studies have shown that it was necessary to use large, minimum fivefold, excess of a polyamine, in order to maximize the conversion of epoxy groups of the GMA resins and minimize the side cross-linking occurring under the influence of amine groups immobilized earlier. Toluene turned out to be the best medium for performing modification of the GMA resins. Resins **GMA-EDA** and **GMA-TAEA** characterized by up to 3.7 and 6.4 wt-% of nitrogen, respectively, could be obtained using this solvent at the temperature of 70-80^{o}C.

Thermal analysis of the resin beads performed before and after their modification showed that the introduction of polyamine units into the structure of the **GMA** resins resulted in an increase in their glass temperature (T_g) by 20-40^{o}C. This finding provided evidence for stiffening in the polymer network within the beads modified with polyamines. This could be a result of partial secondary cross-linking of the modified resins, on the one hand, and/or the effect of mutual hydrogen interactions between the functional groups within the beads of the modified resins (OH groups, amine groups with different orders), on the other hand. The immobilization of the polyamine units did not influence thermal stability of the resins. The decomposition of the resins was still observed only at the temperature above 300^{o}C.

Exploring the usefulness of resins with polyamine units as reactive sorbents for aldehydes, acid chlorides (both acyl and sulphonyl) and diisocyanates, I have studied their reactivity in the medium of several organic solvents. The progress of sorption was examined with chromatographic methods (GC, TLC). The chemical nature of sorption was proved by recording FTIR spectra of the bead isolated from post-sorptive solutions.

I found that the polyamine functionalized resins, used in adequately excessive quantity, generally enabled effective removal of model electrophiles from their solutions even at room temperature. However, in the case of aldehydes, the effectiveness of sorption depended not only on the loading of amine groups and the solvent nature (e.g. alcohols facilitated formation of imines), but also on many other factors, including the structure of aldehyde and the mutual solvent-resin affinity which was decisive for the swelling capacity of the resin. The findings acquired in the course of the studies focusing on sorption of aldehydes were discussed in three articles **H2**, **H3, H7**.

The ability of the resins bearing polyamine units to react with acid chlorides and isocyanates was explored by me in both model solutions and real post-reaction mixtures obtained as a result of a series of acylation and sulphonation reactions using excess amount of an electrophilic reactant. I observed a visible improvement in the purity of the products obtained after treating the post-reaction mixture with the resin containing polyamine units; this was proved with chromatographic and ^{1}H-NMR methods. In most cases, it was possible to observe quantitative removal of a chloride excess from the post-reaction mixtures. This shows that the developed resins are effective sorbents for fast purification of reaction products from the selected electrophilic impurities. The amine resins reacted with acyl chlorides so fast that the acylation products could be purified under the flow conditions using the SPE columns filled with samples of the proper resin. The collected results were discussed in articles **H3** and **H14**.

The techniques of fast and selective purification of reaction products from undesired impurities using reactive sorbents have a particular meaning from the point of view of medicinal chemistry which is directed to synthesis of the library of organic compounds with potential biological activity [9, 26, 27].

The **GMA-EDA**, **GMA-DETA** and **GMA-TAEA** resins turned out to be effective sorbents in relation to some transition metal ions. This was confirmed with a separate study that I conducted using model solutions of Cu(II), Fe(III), Co(II), Mn(II) and Ni(II) salts in methanol and its mixtures with methylene chloride and solutions of Pd(II) salts in THF and in THF-water mixtures.

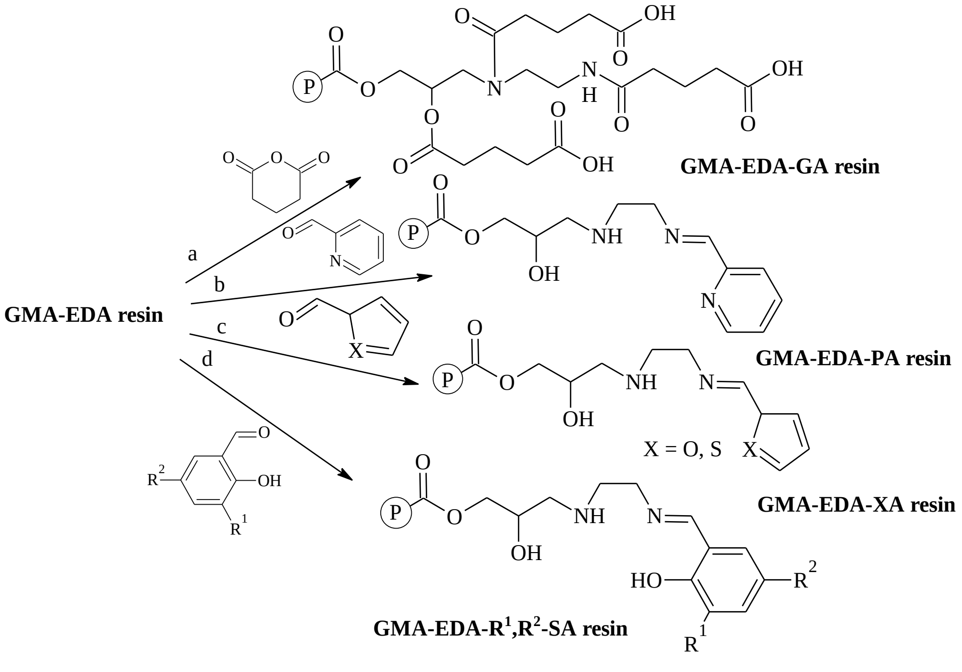
While carrying out the experiments using methanol as a medium which swelled the resins with polyamine units weakly, I noticed an extremely high affinity of the **GMA-EDA** resin to Cu(II) ions, which were removed from the solution nearly quantitatively within 10 minutes. The **GMA-DETA** and **GMA-TAEA** resins stayed practically inactive under the same conditions.

The clearly lower activity of the **GMA-EDA** resin in methanol in relation to Fe(III), Co(II), Mn(II) and Ni(II) ions could be used for selective isolation of copper(II) ions from multicomponent solutions. The reactivity of all the resins in the relation to the explored metal ions increased after the addition of methylene chloride to methanol. This solvent beneficially impacted the resins in terms of their swelling capacity. The results of the study focusing on sorption of Cu(II), Co(II), Mn(II) and Fe(III) ions were discussed in detail in the article published in *J. Appl. Polym. Sci*., **H9**.

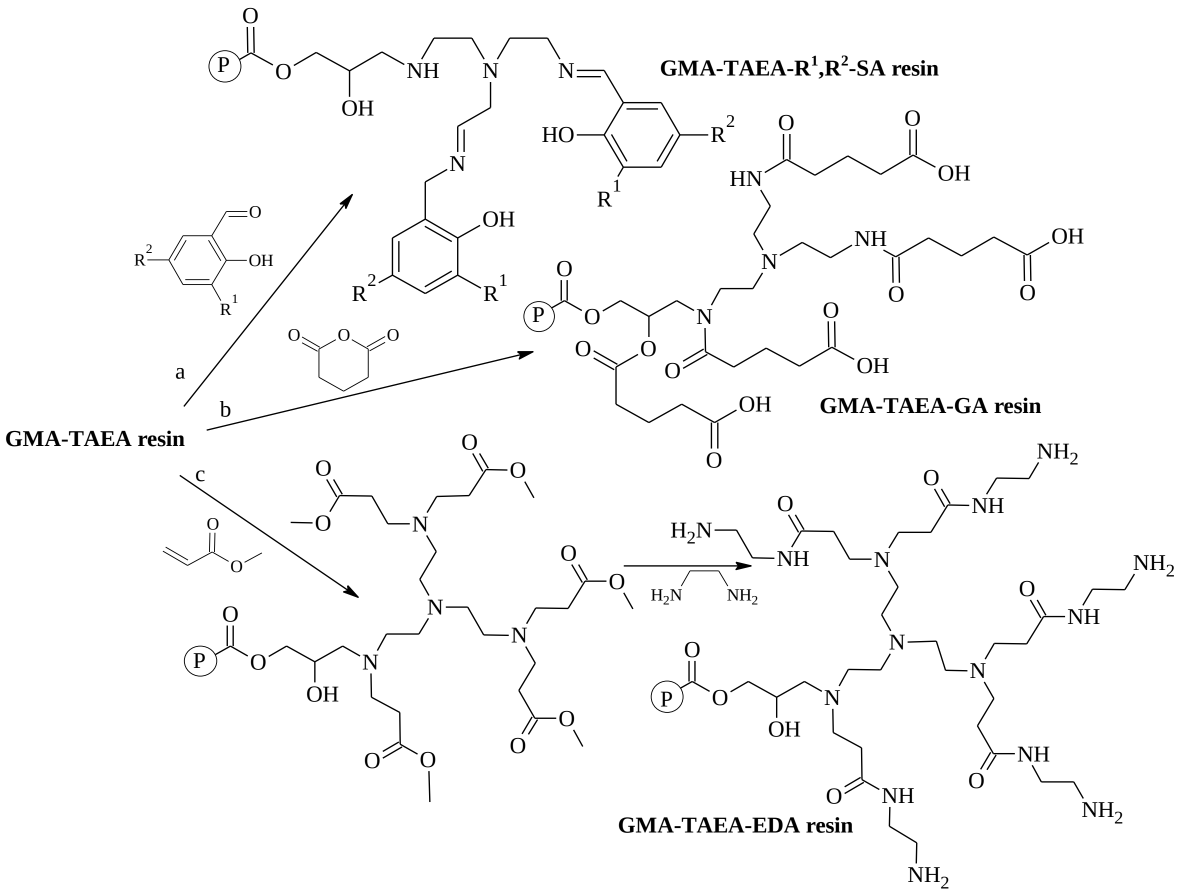
While exploring the affinity of amine resins characterized by the nominal cross-linking degree of 3 mol-% (a cross-linking monomer - DVB or DMGDE) to palladium(II) ions I noticed that the use of the **GMA-EDA** resins in threefold excess to the metal ions resulted in their nearly quantitative removal from the solution in THF within less than 5 minutes. The effectiveness of the resins with **DETA** and **TAEA** functions in removing Pd(II) ions was low under the same conditions. After a small amount of water (at a rate of a few percent) was added to THF, the **GMA-TAEA** resins became very active enabling the total removal of Pd(II) ions within just about 5 minutes. The presence of water also resulted in increased activity of the **GMA-DETA** resins, yet, this increase was not as strong as that observed in the **GMA-TAEA** resins. An excess of water in relation to THF had negative impact on sorptive properties of the poorly cross-linked polymer gels. The peculiar sorption behaviours of Pd(II) ions on the methacrylate-styrene gels bearing **EDA**, **DETA** and **TAEA** functions were discussed in work **H14**.

The works on the use of resins with polyamine functions as scavenging resins were financed with the ministerial grant „*New polyfunctional polymer reagents for selective removal of selected molecules and metal complexes from post-reaction solutions*" [28]; I was the principal researcher in this project.

Simultaneously with the exploration of resins bearing polyamine units used as reactive sorbents for selected electrophiles and transition metal ions, I studied the possibility of using these resins for synthesis of gels with imine (the reaction of NH_2 groups with heterocyclic aldehydes and salicylaldehydes) or polyamide-polycarboxylic (the reaction of amine and hydroxyl groups with glutaric anhydride) systems (Scheme 2 and 3).



Scheme 2. Variants of chemical modification of the **GMA-EDA** resin.



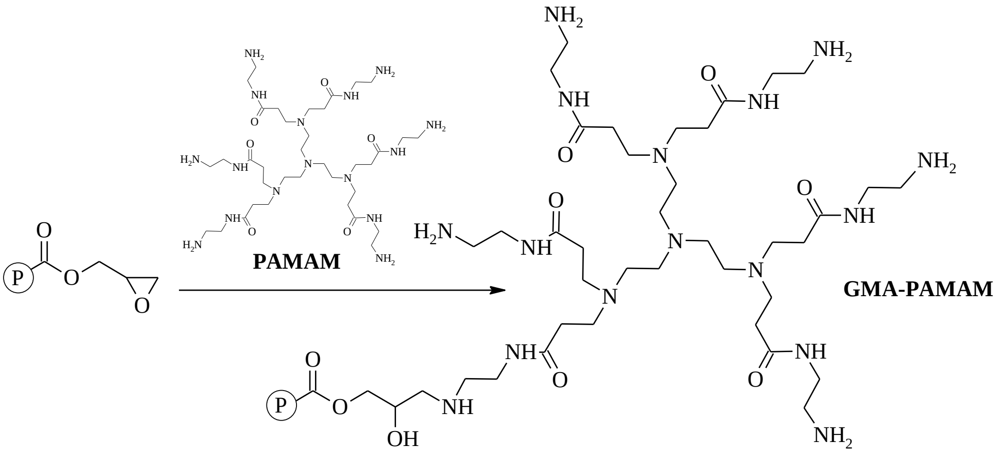
Scheme 3. Variants of chemical modification of the **GMA-TAEA** resin.

In addition, using a two-stage transformation of the **GMA-TAEA** resin in reactions with ethyl acrylate and ethylenediamine I developed a resin with hyperbranched amine-amide-amine system characterized by 13.5 wt-% N (Scheme 3, path c).

The resins obtained as a result of the performed modifications had functional groups which could be utilized for coordination of transition metal ions. For instance, the resins with amine-salicylaldimine functions (**GMA-EDA-SA resins**) were applied for the immobilization of cobalt(II) ions. Their ability to coordinate the metal ions depended on the use of solvent characterized by good swelling properties, e.g. methylene chloride, DMF, THF or toluene. The rate of sorption of Co(II) ions increased visibly when the resin swelling degree increased. The resins were inactive in incompatible solvents, e.g. in strongly polar methanol. The studies on the synthesis of resins with amine-salicylaldimine functions and their sorption ability were financed by ministerial grant [2]. The obtained results were discussed in detail in the article published in *Polimery*, **H2**.

I also synthesized resins bearing a hyperbranched amine-amide-amine system using a direct transformation of the **GMA** resins under the influence of the PAMAM type dendrimer

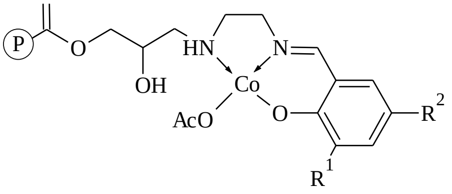
(Scheme 4). The obtained resins showed very high affinity to Pd(II), Ru(III) and Au(III) ions.



Scheme 4. Chemical modification of the GMA resin with the PAMAM type dendrimer.

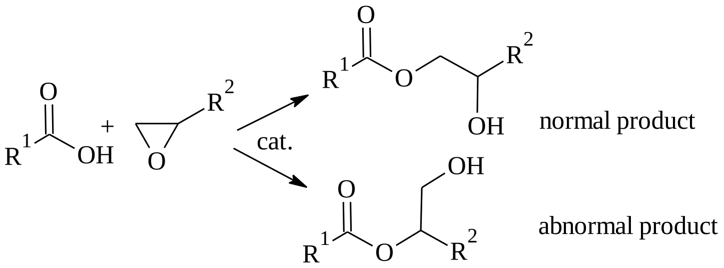
The simplicity of obtaining the reactive polymer materials based on functionalized methacrylates and the possibility of subjecting them to various chemical modifications to obtain systems which can easily coordinate transition metal ions inspired me to explore the developed resins as supports for catalysts.

The resins with amine-salicylaldimine systems were studied first as supports for cobalt(III) catalysts (Scheme 5) for the reactions of carboxylic acids with terminal epoxides (Scheme 6). These reactions are a source of hydroxyalkyl esters which find numerous industrial applications [29]. For instance, hydroxyalkyl acrylates are commonly used as components of coating materials in automotive industry, and the reaction of methacrylic acid with epoxy resins leads to obtaining vinyl-ester resins used in composite materials characterized with very high chemical durability and mechanical strength.



R^1	R^2
H	H
OCH_3	H
tert-Bu	*tert*-Bu
NO_2	NO_2
Cl	Cl

Scheme 5. Polymer supported cobalt catalysts with amine-salicylaldimine moieties.



$R^1 = CH_3$-, CH_2=CH-, $CH_2=C(CH_3)$; $R^2 = CH_3$, CH_2Cl, $C_6H_5OCH_2$

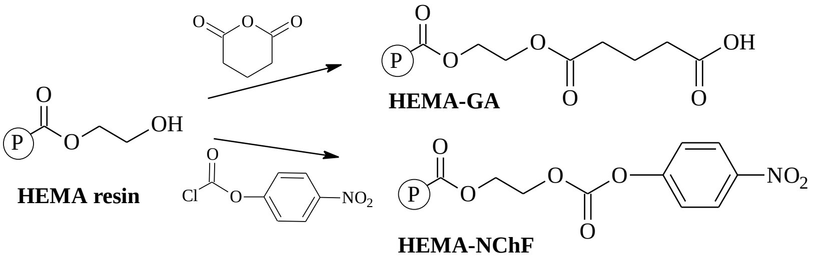
Scheme 6. Reactions of carboxylic acid with terminal epoxides.

The resins bearing different salicylaldehyde units (R^1,R^2 = H, *t*-Bu, NO_2, Cl or R_1=OCH_3, R^2=H) condensed with EDA moieties were used as supports for the cobalt catalysts.

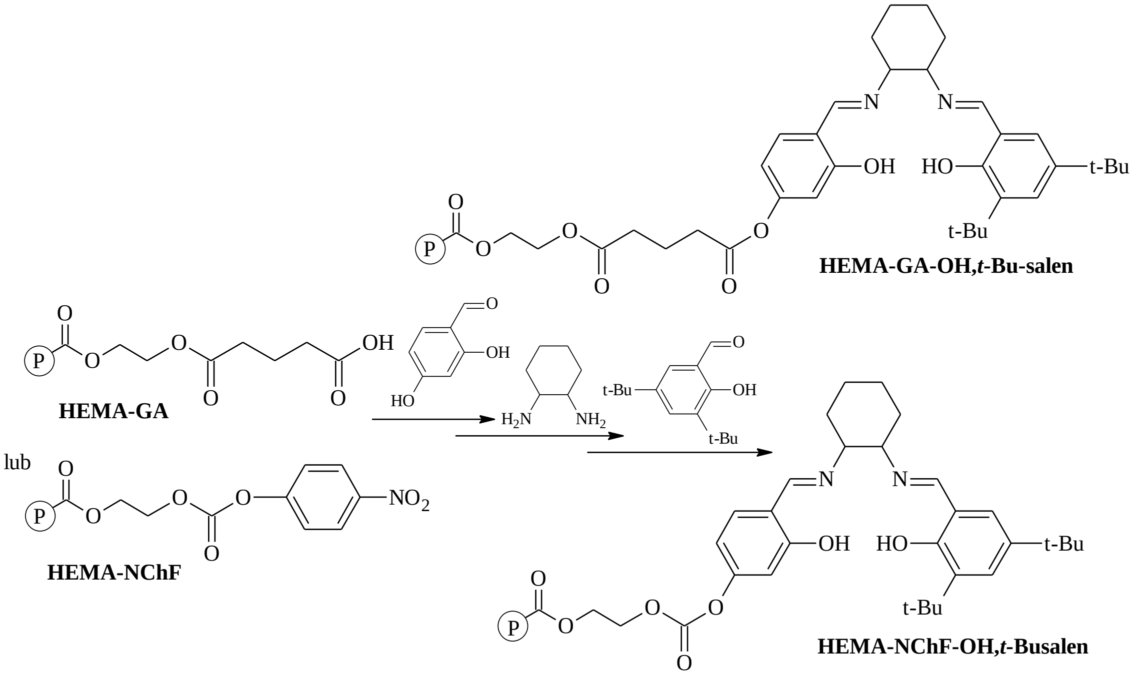
Epichlorohydrin, propylene oxide and glycidyl-phenyl ether, as well as acetic, acrylic, and methacrylic acids were used as model compounds in the catalytic tests. Clearly the highest activity was found for the catalyst with 3,5-di-*t*-butyl-2-hydroxybenzaldehyde units and the lowest for that with 3,5-dinitro-2-hydroxybenzaldehyde ones. Two strong acceptor substituents influenced negatively on the activity of cobalt(III) ions. Cobalt(III) amino-salicylaldimine complexes immobilized on the polymer gel provided high regioselectivity of the epoxide ring opening reactions; normal addition product was formed predominantly. Furthermore, it was found that an increase in the reaction temperature had adverse effect in the catalyst stability under the reaction conditions, intensifying the migration of cobalt ions from the polymer support to the solution. As a result, the catalyst gradually lost the catalytic activity after its reuse. Nevertheless, the catalyst with salicylaldimine system could be used at least three times at 25°C without loss of the activity. The results of the studies focusing on the activity of cobalt complexes immobilized on salicylaldimine resins in the reactions of carboxylic acids with epoxy compounds were described in detail in papers **H4** and **H6.**

The high regioselectivity of the ring opening reactions in terminal epoxides under the influence of carboxylic acids observed for the cobalt catalysts with the monosalicylaldimine systems resulted in the decision to extend the study by including polymer supported catalysts with salen systems. Such catalysts were obtained based on the resins with hydroxyl groups. For this purpose, the selected **HEMA** resins were first modified in the reaction with 4-nitrophenyl chloroformate or glutaric anhydride. The 4-nitrophelycarbonate and glutarate units introduced in this way to **HEMA-NChF** or **HEMA-GA** resins, respectively, facilitated salen units immobilization. This was realized in two ways: by the multi-step construction of a salen system (Scheme 8) or using the direct immobilization of a properly functionalized salen ligand

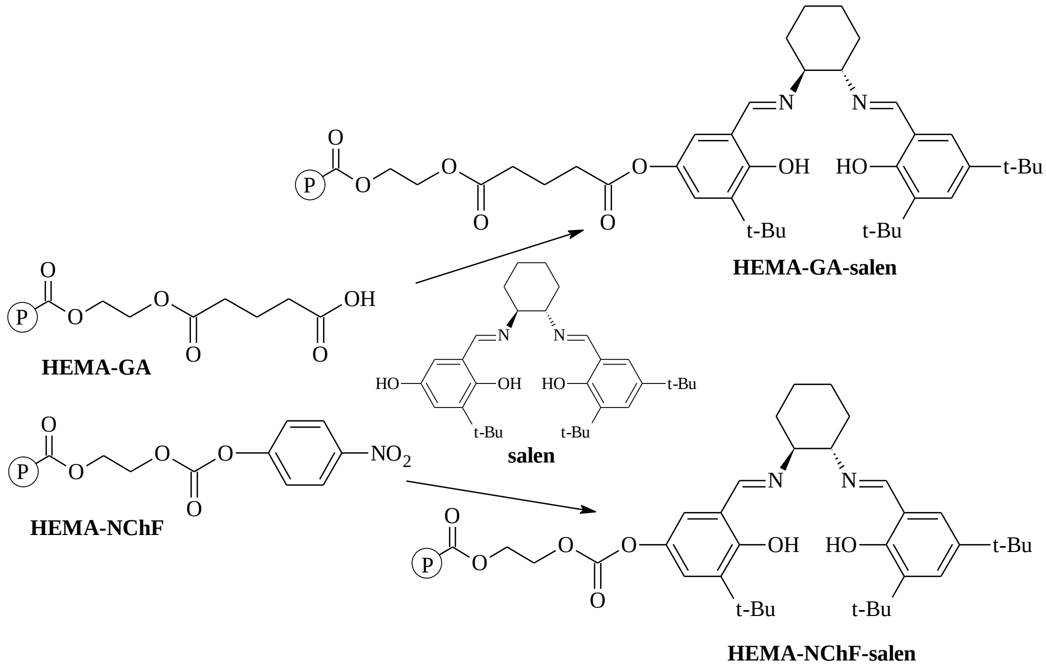
(Scheme 9). The latter method required synthesis of the salen ligand with an additional functional group which could allow to perform its immobilization on the **HEMA-NChF** and **HEMA-GA** resins. I performed the synthesis and immobilization of the ligand following the procedure proposed previously by Jacobsen [30] and Janda [31].



Scheme 7. Initial routes of modification of the **HEMA** resin.



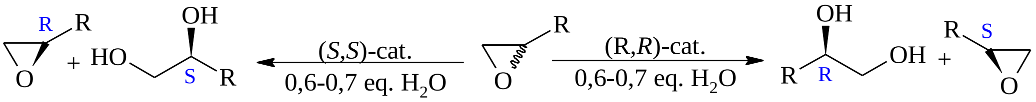
Scheme 8. Multi-stage construction of the salen system on the modified **HEMA** resins.



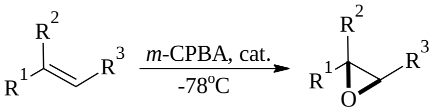
Scheme 9. Immobilization of the unsymmetrically substituted salen ligand on the modified **HEMA** resins

The resins with immobilized salen ligands were used as the supports for cobalt catalysts which were applied in the reactions of carboxylic acids with epichlorohydrin. Among the four types of the obtained salen catalysts, the one which was synthesized as a result of the direct immobilization of the salen ligand on the **HEMA-NChF** resin was most active in the examined reactions. The activity of this catalyst was comparable to that observed in the corresponding homogenous salen catalyst [32]. The activity of the polymer supported salen catalysts turned out to be higher than that observed in the monoimine systems mentioned earlier. The preparation of the polymer supported salen catalysts, their characteristics and the results of catalytic tests in the reactions of carboxylic acids with epichlorohydrin were described in detail in article **H5**.

The use of one of the enantiomers of 1,2-diaminocyclohexane, (*R*,*R*- or *S*,S-), instead of racemic *trans*-1,2-diaminocyclohexane at the stage of synthesis of an unsymmetrically substituted salen ligand made it possible to obtain polymer supports with chiral salen centres (Scheme 9). The supports obtained this way were next used for synthesis of cobalt and manganese salen catalysts which were then studied respectively, in the process of the hydrolytic kinetic resolution (HKR) of terminal racemic epoxides (Scheme 12), and the reaction of epoxidation of substituted olefins (Scheme 13).



Scheme 12. The HKR of terminal *rac*-epoxides.



Scheme 13. Simplified scheme of asymmetric epoxidation of olefins.

The hydrolytic kinetic resolution of racemic terminal epoxides was discovered accidentally by Jacobsen during his work on the reactions of epoxides with benzoic acid in the presence of the chiral salen complex [33]. At present, the HKR process is the best way to prepare enantiomerically pure terminal epoxides and 1,2-diols, also on an industrial scale [34-37].

The methods of asymmetric epoxidation were developed in particular thanks to the discoveries of Sharplessa, Katsuki and Jacobsen [38-40]. The use of properly designed chiral metal complexes as catalysts makes it possible to obtain chiral products enriched with one of the enantiomers from the achiral substrates.

Chiral epoxides belong to the building blocks which are commonly used in pharmaceutical industry. Their relatively high reactivity in the reactions with various nucleophiles and other reagents, such as radicals and Lewis acids, results from the presence of three-membered epoxy ring, and this leads to the possibility to use the epoxy compounds in synthesis of many organic derivatives [41].

The polymer supported chiral Co(III) salen complexes, **HEMA-NChF-salenCo(III)** and **HEMA-GA-salenCo(III),** turned out to be very active as catalysts of the HKR of terminal epoxides and they were stable under applied reaction conditions. The catalytic tests performed for the HKR process of *rac*-epichlorhydrin showed that the activity of the catalysts depended on the functionalization degree of the support and the way of anchoring the salen ligand to the polymer matrix. An increase in the functionalization degree of the support incresed the probability that the HKR process would follow the more advantageous, bimolecular path of the catalytic cycle [42]. However, an excessive increase in the functionalization degree resulted in lower catalytic activity of the complexes. Adequate selection of the functionalization degree made it possible to synthesize a catalyst which can be ranked as one of the most active heterogeneous catalysts of the HKR of *rac*-epoxides described in the literature. It contained salen complex bound with the polymer matrix via the carbonate linker (**HEMA-NChF-salenCo(III)).** This catalyst was far more active than the homogeneous salen complex developed by Jacobsen [33]. Its additional advantage was the possibility of multiple reuse, in ten consecutive reaction cycles, under the same conditions without significant loss in activity. The catalyst was recycled in two manners: without any catalyst regeneration between its reuse and by rinsing the catalyst with acetic acid before its reuse. Additional operation where the catalyst was rinsed with acetic acid was carried out to supplement AcO^- counterions in the immobilized salen Co(III) complexes. It was found that the catalyst was able to keep its very high activity even when the rinsing with acetic acid was not performed. It was observed, however, that the additional regeneration of the catalyst before each next use positively affected its activity. The results of the studies in the HKR process of *rac*-epichlorohydrin in the presence of the developed catalysts were discussed in the article published in *J. Mol. Catal. Chem.-A*, **H11**.

The chiral polymer supported cobalt catalysts also turned out to be useful for the HKR of several other terminal *rac*-epoxides. This was demonstrated by the catalytic studies involving epoxyhexane, epoxyoctane and glycidyl esters (acetate, propionate and butyrate). It was observed that the HKR rate, in the presence of the salen catalysts immobilized on the non-porous polymer gels, depended on the structure of the epoxy compound and the nature of the solvent used in the experiments. A part of the findings was used for preparation of the article published in *Chemik,* **H16**.

The reactions of asymmetric epoxidation in the presence of the Mn(III) salen complexes immobilized on the modified HEMA resin **(HEMA-NChF and HEMA-GA)** were carried out at -78°C, using *m*-chloroperbenzoic acid and N-methylomorpholine N-oxide as an oxidation system (Scheme 13). The product of epoxidation enriched with one of the enantiomers formed in the presence of the developed catalysts. The yield of epoxidation and the excess of the obtained epoxide enantiomer depended on the cross-linking degree of the polymer support and the way of anchoring of the salen complex to the polymer matrix. The use of gels with lower degree of cross-linking and immobilization of the complex via the carbonate linker proved to be more advantageous. The best of the developed catalysts, containing (*R*,*R*)–salen manganese(III) complex, produced (*S*)-epoxystyrene with the enantiomeric excess of about 46% if styrene was used as a reactant. The obtained result was comparable with that described in the literature, e.g. Ref. 31 and 43 [31, 43]. The catalyst did not produce equally satisfactory result for epoxidation of *trans*-β-methylstyrene - only 9% ee *1S,2R-trans*-β-methylepoxystyrene was observed. Epoxidation of indene resulted in obtaining (*1R,2S*)-epoxyindene with 73% ee.

Unfortunately, the chiral salen manganese catalysts based on the methacrylate-styrene gels showed less activity than the homogeneous salen manganese(III) complex described by Jacobsen [44]. Furthermore, it was possible to observe their partial deactivation under the applied epoxidation conditions. As a result, the lower activity was detected when the catalysts were recovered and reused under the same conditions. The results of the studies in the application of the polymer supported chiral salen manganese complexes based on the **HEMA** gels in the asymmetric epoxidation of the selected olefins were published in an article **H8.**

The research into preparation and utilization of the developed polymer supported chiral salen complexes was financed partly by a ministerial grant [45].

Properly functionalized methacrylate-styrene gels turned out to be useful as supports for several other transition metals used in catalytic applications, as well. The unique ability of resins with polyamine and polyacarboxylic functions to bind noble metal ions aroused the interest of prof. A. Drelinkiewicz and dr. D. Duraczyńskiej from Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences and prof. J. Ziółkowskiego and prof. A. Trzeciak from the Faculty of Chemistry, University of Wrocław. The group led by prof. Drelinkiewicz developed palladium catalysts based on the **GMA-EDA and HEMA-GA resins** synthesized by me**.** The catalyst proved to be active in the hydrogenation reactions of acetylene, 2-butyne-1,4-diol and unsaturated carboxylic acids. The results of these joint studies were discussed in five articles, **HD1-5.**

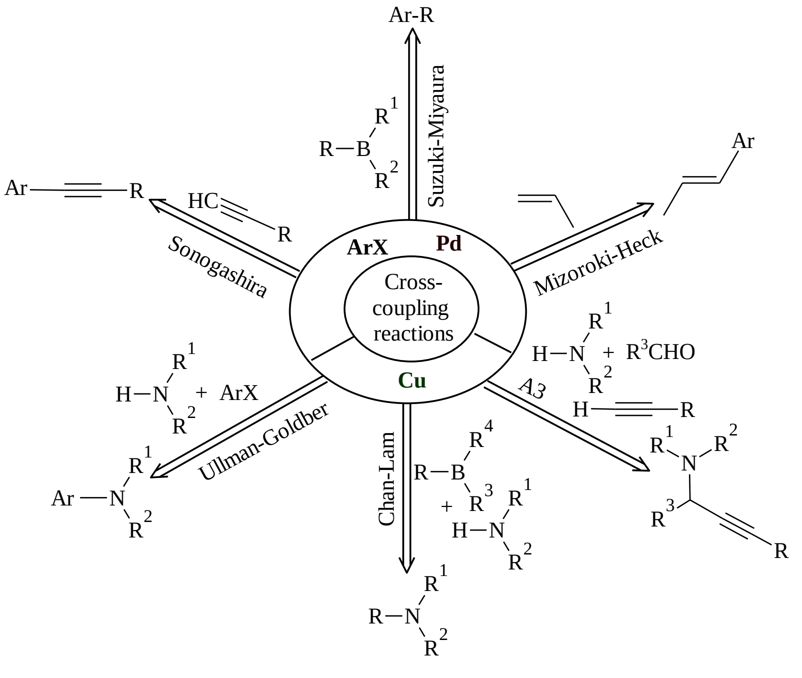
Immobilization of palladium ions on the **GMA-EDA** and **GMA-CHDA** resins enabled the group led by prof. Ziółkowski and prof. Trzeciak to prepare catalysts active in the Suzuki-Miyaura reactions. Two further articles were published as a result of this joint research, **HD7-8**.

Finally, immobilization of Ru(III) ions on the resin with ethylenediamine functions enabled D. Duraczyńska (PhD, from JHICSC of PAS) to obtain a heterogeneous catalyst active in hydrogenation of acetophenone. The findings were reported in a joint article published *React. Funct. Polym.*, **HD6.**

Continued interest in cross-coupling reactions, intensified by the fact that A. Suzuki, R. Heck and E. Negishi received the Nobel Prize in Chemistry in 2010 for „Palladium catalysed cross-coupling reactions in organic synthesis" [46-58], prompted me to start my own research on the preparation of polymer supported palladium and copper catalysts for the needs of cross-coupling reactions.

Catalytic cross-coupling reactions are currently regarded as the most effective methods of formation of C-C and C-N bonds [58-60]. These coupling reactions are often among the key steps in the synthesis of biologically active compounds used in the production of medicinal products, including anticancer drugs, as well as in pesticides production. The C-C cross-coupling reactions are also a source of advanced materials for electronic industry, as well, e.g. materials applied in production of organic-emitting diodes used in super-thin OLED screens.

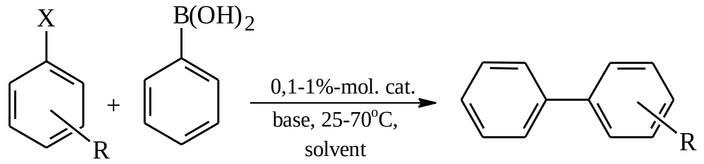
The cross-coupling reactions occur between an organic electrophile, commonly aryl halide, and an organic nucleophile, which differs depending on the type of the reactions. Most commonly, Pd and Cu compounds are the active components of the catalysts used in the cross-coupling reactions (Scheme 14), although numerous examples of the use of other transition metals are also known [61]. The aforementioned transition metals are responsible for the activation of aryl halide or other organic electrophiles. Initially, homogenous catalytic systems were mainly used in the coupling reactions [46]. Yet, due to the cost of catalysts, in particular palladium catalysts, and difficulties encountered in the process of purifying the coupling products from catalyst residuals, at present research mainly focuses on the preparation of heterogeneous catalysts.



Scheme 14. Selected cross-coupling reactions.

Even my first attempts to immobilize palladium(II) ions on the resin with carboxylic groups (**HEMA-GA**), carried out in the framework of a subsidized research project in which I was the principal researcher [28], provided evidence showing a large potential of properly functionalized polymers as supports for catalysts in C-C cross-coupling reactions. I prepared a catalyst which enabled coupling of phenyl boronic acid with arylbromide and aryliodide (Suzuki-Miyaura reaction, S-M) within several hours, even at the temperature of 25°C, with the use of 0.1 mol.-% Pd. The method of synthesizing palladium catalysts based on the resins with carboxylic group was patented, **H17.** Further in-depth research involving the palladium catalysts based on the resins with carboxylic groups revealed, unfortunately, that the high activity was accompanied by a relatively low chemical and mechanical stability of the catalysts. Palladium black was formed under the applied reaction conditions (DMF as a solvent, K_2CO_3 as a base). This significantly diminished the activity of the recovered catalysts during their reuse. Additionally, excessively high affinity of the solvent to the polymer support and the resulting excessive swelling of the resin beads weakened their mechanical strength.

Later, resins with amine (EDA, DETA, TAEA, TETA, DMEDA, DIPEDA, MeOEA) and amine-imine functions were used for the preparation of palladium catalysts. In the latter case, the applied resins contained 2-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde and furfural moieties condensed with EDA or TAEA systems. The catalysts synthesized based on the resins mentioned above were explored in the model Suzuki-Miyaura type cross-coupling reactions (Scheme 15).



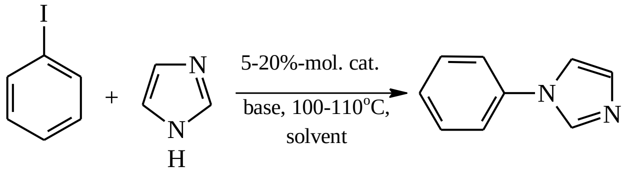
X=Br, I; R=H, CH_3, F, OCH_3, OH, CHO
Scheme 15. Suzuki-Miyaura reaction.

Analyses focused on the effects of reactant, solvent and base nature, as well as temperature in the activity, selectivity and stability of the specific catalysts. It was found that the activity of the catalysts depended on both the structure of amine and aldehyde units. The highest activity was detected in the case of the catalysts with the branched TEAE moieties condensed with 2-pyridinecarboaldehyde. The catalyst bearing 2-thiophenecarboxaldehyde units was visibly less active. The palladium catalysts with polyamine units acted in a slightly different way. The catalysts based on the **GMA-EDA** resins turned out to be the most active.

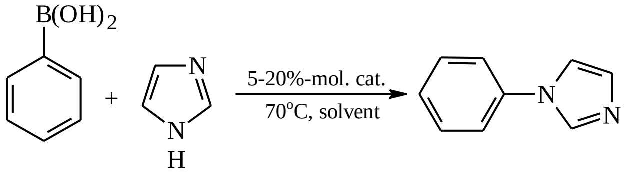
Although, the palladium catalysts with polyamine and amine-imine units were less active than those based on the resins with amide-carboxylic functions, they allowed to obtain the coupling products characterized by higher purity. Unfortunately, the activity of this group of polymer supported palladium catalysts also decreased gradually during the subsequent reaction cycles. The results obtained for the palladium catalysts with amine and amine-imine units were described in detail in the articles **H10** and **H12.**

In order to continue my research focusing on preparation and utilization of polymer supported catalysts, at the next stage I decided to use resins with dendritic, amine-amide-amine functions as the supports for palladium ions. The resins had been developed in course of the subsidized research project mentioned above [28]. Information reported in the literature [62] indicated that the low-molecular PAMAM-Pd(II) complexes can act as effective catalysts in the cross-coupling reactions. Their main disadvantage, however, was a significant loss of catalytic activity observed during attempts to reuse them under the same reaction conditions. The combination of the dendritic PAMAM system with the **GMA** resin proved to be highly effective. The immobilization of palladium ions on the supports with the dendritic functions made it possible to obtain catalysts which, in addition to being highly active, were also stable under the S-M cross-coupling reaction conditions. The best of the catalysts, at the rate of 0.5 mol-% Pd, could be recycled 10 times without significant loss of activity at the temperature of 50-70^{o}C, with the use of isopropyl alcohol and water mixture as a solvent for reagents. Further research involving the developed palladium catalysts with the dendritic systems showed the catalytic activity also in the Mizoroki-Heck reactions between aryl halides and styrene, its substituted derivatives and acrylates. They were active in the Sonogashira reaction between iodobenzene and phenylacethylene, as well. Some of the findings related to the catalysts with the dendritic systems were described in detail in the article published in RSC Advances**, H13.**

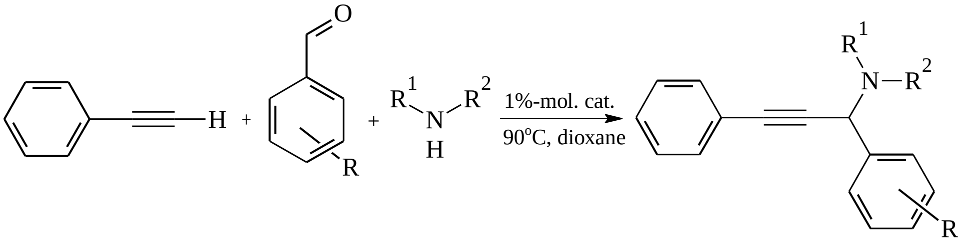
Simultaneously with the work focusing on the preparation of palladium catalysts for C-C cross-coupling reactions I did research on the preparation of polymer supported copper catalysts for C-N coupling reactions. The developed catalysts were studied initially in the model coupling reactions of iodobenzene with phenyl boronic acid (Ullmann-Goldberg reaction (Scheme 16) and imidazole with phenyl boronic acid (Chan-Lam reaction) (Scheme 17). Afterwards, my research was expanded to include A3 coupling reactions (Scheme 18).



Scheme 16. Ullmann-Goldberg reaction.



Scheme 17. Chan-Lam reaction.



Scheme 18. A3 coupling reactions.

Even the first catalytic tests performed for the coupling reaction of iodobenzene and imidazole showed that immobilization of copper(II) ions on resins bearing polyamine and amino-salicylaldimine functions (Table 1) allowed to obtain polymeric materials catalytically active in the reaction of C-N bond formation. The catalysts bearing polyamine systems were less active than those with amino-salicylaldimine functions. I observed only slight differences in the activity of the explored polymer supported amine-salicylaldimine complexes in the reaction of iodobenzene and imidazole despite the modification of the ligand structure by introducing different acceptor and donor substituents at positions 3 and/or 5 of the salicylaldehyde unit. Unfortunately, the catalysts were found with insufficient chemical stability under the applied, harsh reaction conditions (DMSO as a solvent, KOH as a base, and temperature of 110°C) (Table 2). The use of phenylboronic acid rather than iodobenzene enabled the C-N bond formation in the presence of the same catalysts under much milder reaction conditions. The use of ethanol as a “green” solvent and K_2CO_3 as a base, or even performing the coupling reaction between phenylboronic acid and imidazole without any additional basic reagent, led to obtaining N-phenylimidazole with nearly 100% yield within 3-5 hours.

I observed the extremely beneficial effect of the electron acceptor substituents (NO_2 and F) at positions 3 or 3 and 5 of the salicylaldehyde unit, in the activity of the polymer supported copper catalysts in the coupling reaction of imidazole with phenylboronic acid. The presence of CH_3 group at position 3 in the aldehyde unit practically deactivated the relevant polymer supported copper(II) complex in this reaction (Table 3).

Table 1 Polymer supported copper catalysts.

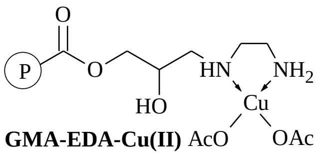
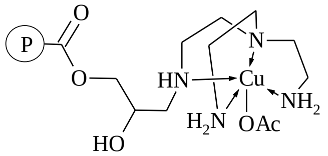
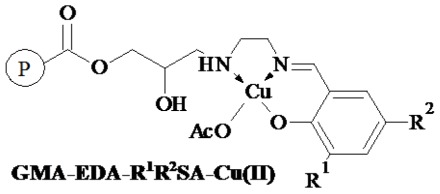
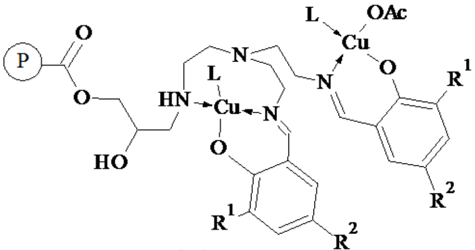
Cu(II) complex	Aldehyde abbreviation	R^1	R^2	Cu loading mmol/g	Cu loading %
 **GMA-EDA-Cu(II)**				0,91	5,8
 **GMA-TAEA-Cu(II)**				0,79	5,0
 **GMA-EDA-R¹R²SA-Cu(II)**	SA	H	H	0,80	5,1
	3-MeOSA	OCH_3	H	0,66	4,2
	3,5-di-*t*-BuSA	*t*-Bu	*t*-Bu	0,64	4,1
 **GMA-TAEA-R¹R²SA-Cu(II)**	SA	H	H	0,91	5,8
	3-MeOSA	OCH_3	H	0,64	4,1
	3-MeSA	CH_3	H	0,64	4,1
	5-FSA	H	F	0,91	5,8
	3,5-di-FSA	F	F	0,81	5,2
	5-NO_2SA	H	NO_2	0,54	3,4
	3,5-di-NO_2SA	NO_2	NO_2	0,60	3,8

Table 2. Results of the C-N coupling reaction between imidazole (1.5 eq) and iodobenzene (1 eq.); KOH (2 eq), DMSO, 110^oC.

Catalyst			Time, h	Yield,* %
GMA-EDA- Cu(II)			5	97
GMA-TAEA-Cu(II)			9	94
GMA-EDA-R^1R^2SA-Cu(II)	R^1	R^2		
	H	H	5	94
	OCH_3	H	9 (24)	94 (99)
	t-Bu	*t*-Bu	8 (24)	91 (98)
GMA-TAEA-R^1R^2SA-Cu(II)	H	H	5 (9)	96 (99)
	OCH_3	H	5 (24)	90 (99)
	CH_3	H	4 (24)	85 (97)
	NO_2	H	24	93

* Yield determined chromathographically.

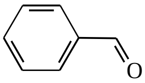
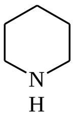
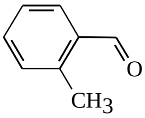
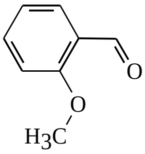
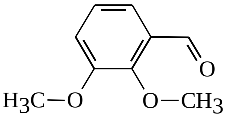
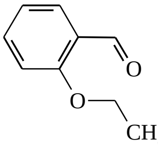
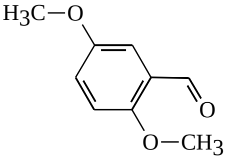
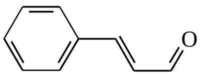
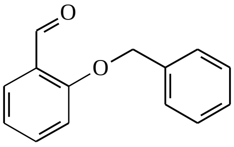
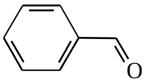
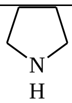
Table 3. Results of the C-N coupling reaction between imidazole (1.5 eq) and phenylboronic acid (1 eq.); solvent – ethanol, 70^oC.

Catalyst			Base	Time, h	Yield,* %
GMA-EDA- Cu(II)			K_2CO_3	24	27
			-	8	99
GMA-TAEA-Cu(II)			K_2CO_3	24	22
			-	24	99
GMA-EDA-R^1R^2SA-Cu(II)	R^1	R^2			
	H	H	K_2CO_3	24	38
			-	10	99
GMA-TAEA-R^1R^2SA-Cu(II)	H	H	K_2CO_3	24	99
			-	24	32
	OCH_3	H	K_2CO_3	24	41
			-	24	40
	CH_3	H	K_2CO_3	24	9
			-	24	-
	F	H	K_2CO_3	12 (24)	87 (99)
	F	F	K_2CO_3	8 (24)	77 (99)
			-	8	99
	NO_2	H	K_2CO_3	12 (24)	88 (99)
			-	5	99
	NO_2	NO_2	K_2CO_3	12 (24)	90 (99)
			-	3 (7)	77 (99)

*Yield determined chromathographically.

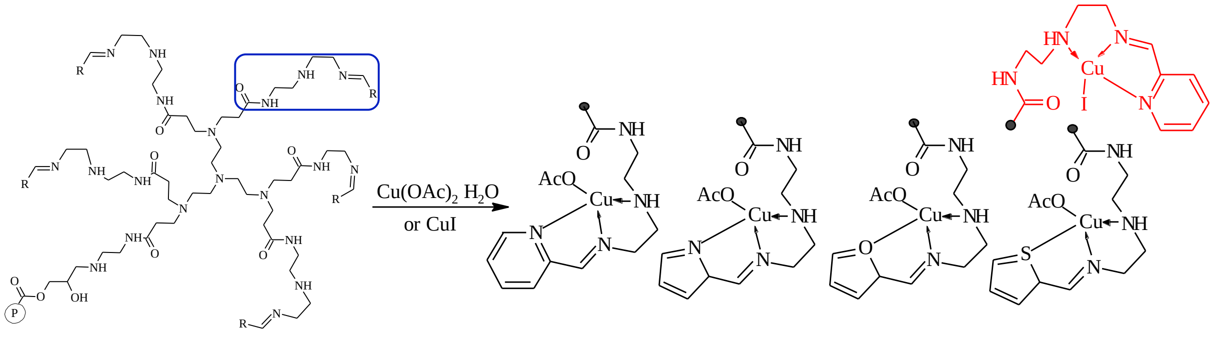
The polymer supported copper(II) complex with the amine-salicylaldimine system (**GMA-EDA-SA-Cu(II)**) proved to be catalytically active in the A3 coupling reactions between aldehyde, amine and terminal alkyne. These three-component reactions are a source of propargyloamines which are important intermediate products in the synthesis of many biologically active substances [63-65]. While exploring the model A3 coupling reaction in the presence of the aforementioned copper(II) complex I noticed that, besides desired propargiloamine, a side product of the homo-coupling of phenylacetylene was also formed under the applied reaction conditions. The formation of this side product could be minimized by optimizing the reaction conditions. The polymer supported copper catalyst with the amine-salicylaldimine units was successfully applied five-times in the reaction of phenylacetylene, benzaldehyde and piperidine performed in dioxane at 80°C. There was no significant decrease in its activity. The catalyst could also be successfully used in the reactions of a series of mono- and di-substituted benzaldehydes and several other secondary amines. The high yields of the proper propargyloamines were obtained in these reactions (Table 4).

Table 4. Results of the A3 coupling reaction of aldehyde, amine and phenylacetylene; cat. – **GMA-EDA-SA-Cu(II)** (1%-mol.), solvent – dioxane, 80°C.

Aldehyde	Amine	Time, h	Aldehyde conversion, %
		10 (24)	82 (99)
		24	89
		10 (24)	92 (97)
		24	88
		24	77
		24	89
		3	99
		24	94
		24	96

*Conversion determined chromathographically.

I also obtained promising results in the A3 coupling reactions for the catalysts prepared by immobilization of copper(II) ions on the resins with dendritic units (Scheme 19, Fig. 1). Currently, this research is continued with the use of various amine and aldehyde reagents.



Scheme 19. Synthesis of the polymer supported copper catalysts with dendritic units.

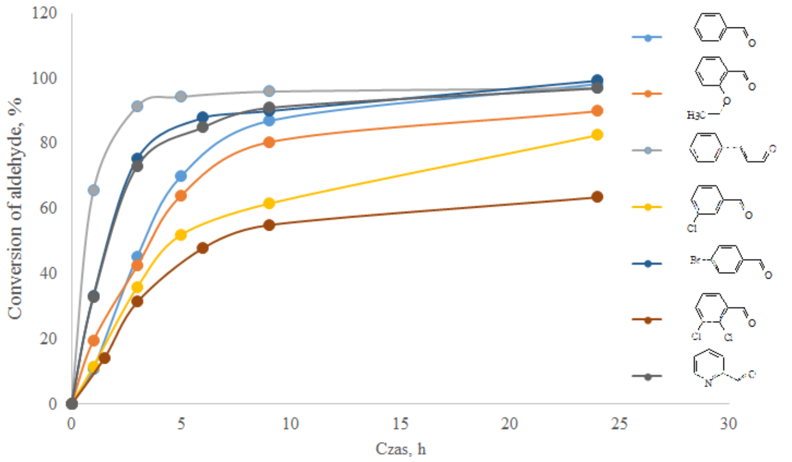


Fig. 1. Results of the A3 coupling reaction of aldehyde, morpholine and phenylacetylene in the presence of the polymer supported copper catalysts with dendritic units (1 %-mol.) in dioxane at 90°C.

The findings of the completed studies focusing on the synthesis of the polymer supported copper catalysts, their characterization and catalytic tests in the C-N and A3 coupling reactions are currently being worked out for the needs of two manuscripts of articles related to this subject.

In order to develop new polymer supports for catalytic applications, I recently decided to slightly modify the morphology of the metacrylate-styrene polymers produced based on glycidyl methacrylate or 2-hydroxyethyl methacrylate. For this purpose, I made an attempt to use water-in-oil emulsions (w/o) and toluene dispersion of Fe_3O_4 nanoparticles as modifiers of the dispersed phase in the process of suspension polymerization. The nanoparticles were prepared using the method of co-precipitation of Fe^{2+} and Fe^{3+} ions under the influence of concentrated ammonia solution and subsequently hydrophobized with oleinic acid. As a result, it was possible to obtain stable dispersion of Fe_3O_4 nanoparticles in toluene. By using emulsions produced by combining water solution of Tween-80 emulsifier with a mixture of 2-hydroxyethyl methacrylate, styrene, and divinylbenzene dissolved in a mixture of cyclohexanol and octanol, I was able to obtain polymer particles characterized by the specific surface area of 47 m^2/g. Findings of these studied were reported in *Polimery* magazine, **H15.** The use of the toluene dispersion of Fe_3O_4 nanoparticles for dilution of the monomer mixture resulted in obtaining polymer particles characterized by multi-hollow architecture (Photo 1). The developed polymer materials are currently explored as supports for the catalysts for the model C-C cross-coupling reactions. This problem is being investigated in the framework of two doctoral studies carried out under my guidance. The obtained results will be used for preparing further articles.

Image 1. SEM image of the **GMA resin** obtained using toluene dispersion of Fe_3O_4 nanoparticles.

Summary

The methacrylic terpolymers bearing epoxy and hydroxyl groups, following their chemical modification, proved to be very interesting reactive sorbents which, on the one hand, can be utilized for purification of reaction products, e.g. from excess of some electrophilic reactants or homogeneous catalysts, and on the other hand can be applied as supports for catalysts based on transition metals. Based on these it was possible to obtain catalysts active in the reactions of epoxide ring opening, including the HKR process of terminal epoxides, epoxidation, hydrogenation (cooperation with Jerzy Haber Institute of Catalysis and Surface Chemistry), C-C cross-coupling (partly in cooperation with FCh WU) and in C-N coupling, as well as A3 coupling.

The findings related to preparation, characterization and application of the developed reactive polymer materials provided data for 24 publications and 1 patent, including 16 articles (12 listed in JRC database) connected with the scientific achievement entitled “Polymer gels for sorptive and catalytic purposes”, indicated for the needs of the habilitation proceeding. The results were also presented many times at scientific conferences.

3. Presentation of other scientific and research accomplishments

After obtaining the doctoral degree in chemical sciences and taking up the position of Assistant Professor at the Department of Industrial and Materials Chemistry, at Rzeszów University of Technology, in 1992, I continued research related to the topic of my doctoral dissertation. In our research team we were particularly interested in the use of chromium(III) compounds as catalysts in epoxide ring opening reactions. Our research initially focused on the effects of common chromium(III) salt, chromium(III) acetate, in kinetics as well as regioselectivity of epoxide ring opening under the influence of carboxylic acids occurring in solvent free systems. This research was partly performed in the framework of the project entitled “Development of modifier technology for epoxy and polyester resins”, commissioned by Organika-Sarzyna Chemical Plant in Nowa Sarzyna, and carried out at the Department of Industrial and Materials Chemistry in 1992-1994, and under a subsidized study entitled “Unsaturated polyester resins with reduced content of styrene”. By using the chromium catalyst, we were able to obtain adducts of methacrylic acid with EPIDIAN 6 epoxy resin characterized by relatively low viscosity; this enabled reduction in the quantity of styrene added to the resin before its application. The developed method of synthesis of low-styrene vinyl ester resin has been patented [66]. Unfortunately, due to environmental restrictions we failed to implement the developed technology on an industrial scale.

The research focusing on reactions of carboxylic acid with epoxy compounds was then expanded to include other reactants and the reactions in solvents, both polar and nonpolar. Other catalytic systems including chromium(III), iron(III) and cobalt(III) ions were also explored. The research was financed by the ministerial grant entitled “Application of chromium, cobalt and iron complexes in selected transformations of epoxy compounds”, in which I was the main researcher [67].

The findings related to reactions of carboxylic acid with epoxy compounds in the presence of homogenous catalysts based on selected transition metal ions, to which I contributed, were reported and discussed in 11 articles listed in JRC database [68-78]. The results were also presented at a number of scientific conferences.

From 1998 to 2000 I also collaborated with prof. A. Szymański from the Department of Physics, at Rzeszów University of Technology; I worked on developing methodology of measurement of cross-linking in epoxy resins with the use of electrical methods. Two articles were published as a result of this joint research project [79, 80].

In the period of 2000-2008 together with colleagues from the Department of Industrial and Materials Chemistry I was involved in research focusing on such issues as: the synthesis of hyperbranched compounds [81], formation of ceramics-polymer composites [82], and synthesis of chiral derivatives of propranolol [83]; these were financed by several ministerial grants.

More recently, in addition to the research in reactive polymer gels, described above, I also carried out studies focusing on core-shell systems with magnetic particles. My collaboration with M. Parlińska-Wojtan, D.Sc, from the Faculty of Physics, at the University of Rzeszów (currently employed at Institute of Nuclear Physics, at the Polish Academy of Sciences in Cracow), who is a specialist in microscopic techniques (SEM and TEM), resulted in a manuscript for an article discussing synthesis and characteristics of inorganic-polymer composites obtained with the use of two techniques - seed emulsion polymerization of a mixture of styrene, divinylbenzene and glycidyl methacrylate and seed precipitation distillation polymerization of a mixture of glycidyl methacrylate and divinylbenzene [84].

In the future, I intend to continue research in inorganic-polymer nanocomposites and their application. Inorganic-organic composites are interesting in particular from the point of view of their applications in catalysis.

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Agnieszka Bukowska