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„Nitroxides in the preparation of functional nanomaterials"

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS SUBMITTED FOR THE
HABILITATION PROCEDURE

Warsaw 2017

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1. **Name and Surname:** Elżbieta Megiel

2. **Scientific diploma and degrees**

PhD in chemistry – 1999, University of Warsaw, Faculty of Chemistry. Doctoral thesis, entitled: „*The studies of excess volumes for selected group of non-electrolytes with low molecular weights*" Supervisor: Prof. dr hab. Teresa Kasprzycka-Guttman,

MSc in chemistry 1994, University of Warsaw, Faculty of Chemistry, Supervisor: Prof. dr hab. Teresy Kasprzyckiej-Guttman, thesis entitled: „*The enthalpies of mixing for binary systems pyridine base + o-xylene*"

3. **Employment**

lecturer, University of Warsaw, Faculty of Chemistry, October 2013-present

adjunct, University of Warsaw, Faculty of Chemistry, October 2001- September 2013

assistant, University of Warsaw, Faculty of Chemistry, October 2000 – September 2001

4. Indication of achievement resulting from Article 16 Section 2 of the Act on University Degrees and the University Title and University Degrees and the University Title in the Field of Arts of March 14, 2003 (Journal of Laws No. 65, item 595, with later amenments):

4.A Title of scientific achievement

"Nitroxides in the preparation of functional nanomaterials"

4.B. The list of publications constituting the scientific achievement

* - corresponding author

wp – papers completed without participation of workers with professor title and dr hab.
degree

IF – Impact Factor (at the time of publication)

	IF	Number of citations (Web of Science)
H1. E. Megiel,[*] A. Kaim, "Factors Influencing the C-ON Bond Strength of the N-Alkoxyamines in the Styrene-Acrylonitrile-TEMPO Copolymerization System." Journal of Polymer Science Part A: Polymer Chemistry (2008) 46, 1165 - 1177.	3,821	10

My contribution to this work consisted of designing and performing the entire studies including all calculations, summarizing of results, preparing the manuscript, as well as publishing the paper.

I declare my percentage contribution to be equal to 90%.

	IF	Number of citations
H2. E. Megiel,[*] A Kaim, M. K Cyrański, "Theoretical and experimental studies on stability of the CON bond in new ketone functionalized N-alkoxyamines." Journal of Physical Organic Chemistry (2010) 23, 1146 – 1154.	1,478	3

My contribution to this work consisted of designing and performing the most studies (except X-ray measurements), summarizing of all results, preparing the manuscript (except this part which describes X-ray measurements) and publishing the paper.

I declare my percentage contribution to be equal to 80%.

	IF	Number of citations
H3. A. Kaim, J. Szydłowska, P. Piotrowski, **E. Megiel,**[*] "One-pot Synthesis of Gold Nanoparticles Densely Coated with Nitroxide Spins" Polyhedron (2012) 46, 119-123.	1,813	6

My contribution to this work consisted of designing and performing the most studies including syntheses, characterization of the synthesized materials (using UV-vis spectroscopy, TEM microscopy, thermal analyses TG, DSC), furthermore I summarized all results, prepared the manuscript (except the Introduction fragment and this fragment which describes EPR studies), Supplementary Materials and I led the process toward publication of the paper.

I declare my percentage contribution to be equal to 70%.

H4.[WP] **E. Megiel**, "Application of New Unimolecular Initiator in the synthesis of the (α,ω) Ketone Functionalized Polystyrene In Nitroxide Mediated Polymerization"

Journal of Applied Polymer Science (2013) 127, 4858 - 4864.
I declare my percentage contribution to be equal 100%.

1,640   1

H5. O. Swiech, R. Bilewicz, **E. Megiel,**[*] "TEMPO coated Au nanoparticles: Synthesis and tethering to gold surfaces" RSC Advances (2013) 3, 5979-5986.

3,708   10

My contribution to this work consisted of designing the most studies including designing and performing of nanoparticles syntheses, physicochemical characterization of the synthesized materials (using UV-vis spectroscopy, TEM microscopy, TG, XPS and EDS spectroscopy), furthermore I summarized all results, prepared the manuscript (except these parts which describe electrochemical measurements). I also prepared Electronic Supplementary Information and I led the process toward publication of the paper.
I declare my percentage contribution to be equal to 70%.

H6.[WP] K. Zawada, W. Tomaszewski, **E. Megiel**[*], „A smart synthesis of gold/polystyrene core-shell nanohybrids using TEMPO coated nanoparticles" RSC Advances (2014), 4, 23876-23885.

3,840   9

My contribution to this work consisted of designing the entire studies including the nanomaterials syntheses and methods for characterizing the synthesized materials (UV-vis spectroscopy, TEM microscopy, thermal analysis TG, XPS spectroscopy), I also summarized all results, prepared the manuscript (except these parts which describe EPR and SEC measurements), Electronic Supplementary Information and I led the process toward publication of the paper.

I declare my percentage contribution to be equal to 80%.

H7.[WP] M. Gozdziewska, G. Cichowicz, K. Markowska, K. Zawada, **E. Megiel,**[*] "Nitroxide-coated silver nanoparticles: synthesis, surface physicochemistry and antibacterial activity" RSC Advances (2015), 5, 58403–58415.

3,289   6

My contribution to this work consisted of designing the entire studies including the nanoparticles syntheses (the syntheses have been carried out by my students: Gozdziewska M. Cichowicz G during their works on BSc and MSc degrees under my supervision), furthermore I performed physicochemical characterization of the synthesized materials using UV-vis spectroscopy, TEM microscopy, XPS, thermal analyses, I also summarized all results and prepared the manuscript (except these

fragments which describe EPR and microbiological measurements). I also prepared Electronic Supplementary Information and I led the process toward publication of the paper. **I declare my percentage contribution to be equal to 70%.**

H8.[wp] P. Krystosiak, W. Tomaszewski, **E. Megiel,**[*] "High-density polystyrene-grafted silver nanoparticles and their use in the preparation of nanocomposites with antibacterial properties" Journal of Colloid and Interface Science 2017, 498, 9-21.

4,233

My contribution to this work consisted of designing the entire studies including the nanoparticles syntheses (these syntheses have been performed by Krystosiak P. during his works on BSc and MSc degrees under my supervision). Furthermore I performed physicochemical characterization of the synthesized materials using UV-vis spectroscopy, TEM microscopy, thermal analyses, summarized all results and prepared the manuscript as well as Supplementary Material. I also led the process toward publication of the paper.
I declare my percentage contribution to be equal to 80%.

H9.[wp] **E. Megiel**, „Surface modification using TEMPO and its derivatives" Advances in Colloid and Interface Science, (2017), DOI:10.1016/j.cis.2017.08.008, in press.

7,223

Review paper.

I declare my percentage contribution to be equal 100%.

Total Impact Factor H1-H9	31,045	45

Mean IF per publication
(at the time of publication).   3,449

4.C The description of scientific goal and the results in the publications constituting scientific achievement.

Nitroxyl radicals (NRs), also called nitroxides, is a class of compounds that contain >N-O• moiety with unpaired electron delocalized between the nitrogen and oxygen atoms. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is undoubtedly the most prominent compound among stable nitroxides. The high stability of TEMPO and its derivatives (**Figure 1**) mainly results from the following phenomena: (1) the delocalization of one unpaired electron over the nitrogen-oxygen bond, (2) an inability to disproportionate to the corresponding nitrone and hydroxylamine because of a lack of α-hydrogen atoms, and (3) an inability to recombine with itself because of steric hindrance of methyl groups.[1]

The stable nitroxyl radicals are extensively used as oxidation catalysts for organic synthesis, mediators for Nitroxide Mediated Radical Polymerization (NMRP), spin probes for biochemical research, magnetic resonance imaging (MRI) contrast agents, dynamic nuclear polarization (DNP) agents for NMR spectroscopy, building blocks for the preparation of organic magnets and electrode materials for organic batteries.[1]

Furthermore, during the last 15 years, many reports have been published on antioxidant properties of NRs. It was well-admitted that the NRs are mimetics of the enzyme superoxide dimutase (SOD), they inhibit Fenton and lipid peroxidation reactions.[1] Due to the antioxidative properties, the NRs are also intensively studied as potential radioprotective agents.[2]

Recently, antitumor activity of NRs has also been proved. Interestingly, the NRs exhibit opposite effect on cancer cells (prooxidative) and on normal cells (antioxidative).[2]

The studies presented in this dissertation focus on the design of NRs' derivatives and their applications in the preparation of functional nanomaterials for catalytic, sensoric and medical purposes.

The aim of the publications constituting the scientific achievement was developing of novel methods for the preparation of functional nanomaterials using nitroxides.
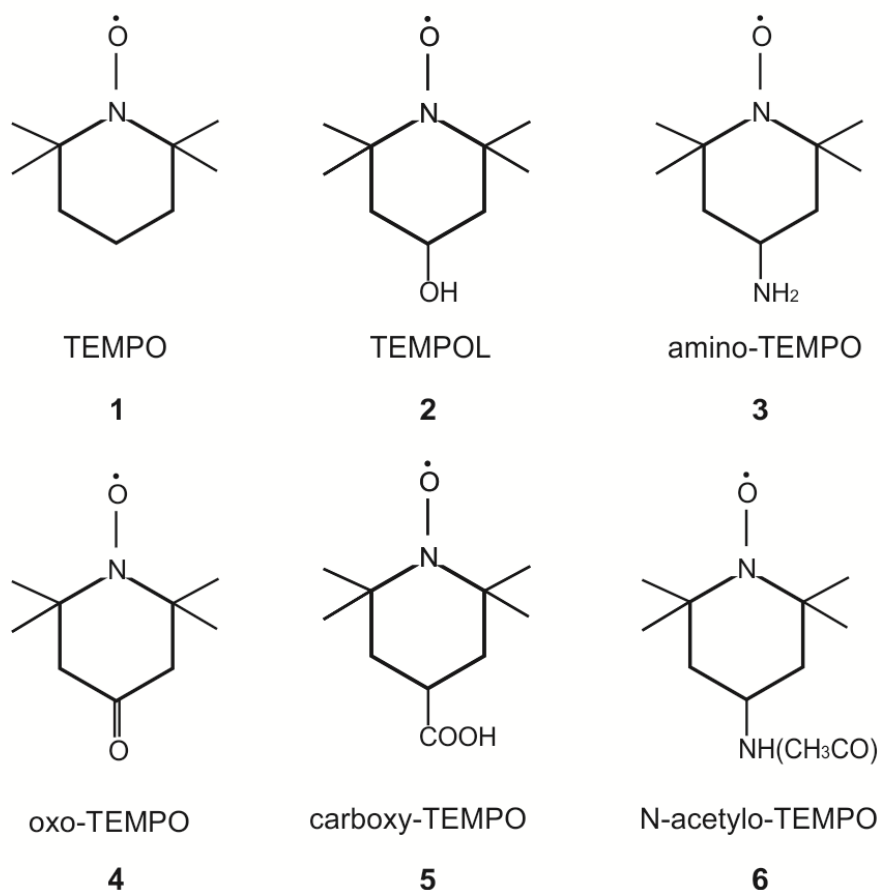
Figure 1. The structure of TEMPO and its selected derivatives.

The series of publications which constituting the scientific achievement submitted for the habilitation procedure includes 8 of original papers (**H1-H8)** and 1 review paper (**H9**) which presents the achievement compared to the data reported in the literature so far.

My studies described in this series of publications concern three interconnected research areas:

I. **The design of novel unimolecular initiators for NMRP (the publications: H1, H2, H4),**

II. **Surface modification of nanomaterials using nitroxides (the publications: H3, H5, H7, H9),**

III. **Application of nanoparticles coated with nitroxides in the preparation of functional polymer materials using NMRP (the publications: H6, H8, H9).**

Introduction

Nitroxide Mediated Radical Polymerization (NMRP) is a one of controlled radical polymerization (CRP) techniques which was first reported by Solomon, Rizzardo and Cacioli in 1985 (in European patent application).[3] Generally, NMRP is based on a reversible coupling reaction (activation and deactivation) between a growing propagating polymer chain ($CH_3P\bullet$) and nitroxyl radicals (as a mediator), for example TEMPO (**Figure 2**), which establish a dynamic equilibrium between dormant and active forms of a growing polymer chain.
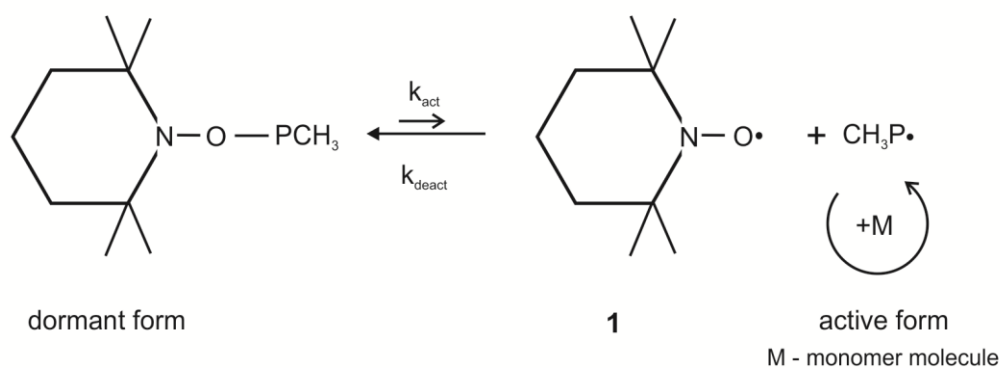

Figure 2. The scheme of NMRP mediated by TEMPO radical.

Lowering of macroradical concentration in the polymerization system significantly suppresses termination processes and achieves controlled growth of uniform polymer chains; thus polymers with narrow polydispersities can be synthesized. The molecular weight and architecture of (co)polymers, prepared by using NMRP can, therefore, easily be designed. The dormant form, also called N-alkoxyamine, contains a thermally or photochemically unstable C-ON bond, which can decompose homolytically into the active form of propagating polymer chain and the stable nitroxyl radical. To achieve the controlled growth of polymer chains, the activation/deactivation equilibrium should be significantly shifted toward the dormant form.

In the case of NMRP, similarly to other CRP techniques, the termination processes cannot be fully suppressed (as it is possible in the case of living anionic polymerization); however, they are appreciable diminished in comparison with the conventional radical polymerization.

NMRP enables the preparation of chain-end functionalized homopolymers with a narrow polydispersities as well as copolymers with well-defined and also complex architecture (e.g. block, graft, gradient, hyperbranched copolymers). Thus, this technique can be used as an excellent tool for the preparation of functional polymer (nano)materials with specific properties that predispose them to a particular applications such as catalytic, sensoric, medical, electronic and others.[4]

The initiation step in NMRP can be performed by using conventional initiator such as benzoyl peroxide (BPO) or 2,2'-azoisobutyronitrile (AIBN) (bimolecular system) or using N-alkoxyamine as an unimolecular initiator which homolytically decomposes into both the initiating radical and the nitroxide (**Figure 2**). Notably, the utilization of unimolecular initiators gives better control over molecular mass and polydispersity than bimolecular initiating system.[5] However, in order to achieve successful initiation and well polymerization control, the N-alkoxyamine must meet several requirements: 1) the C-ON bond in the alkoxyamine molecule should be properly thermally unstable, 2) as a result of the homolytic decomposition of this bond stable non-initiating radical (nitroxyl radical) should be generated and the radical which can initiate the polymerization (alkyl/aryl radical), 3) the generated stable nitroxide should participate insignificantly in disproportionate reaction as it leads to the termination of the polymerization. The disproportionate reaction consisting in β-hydrogen atom transfer from propagating polymer radical to the nitroxide and formation of hydroxylamine and polymer chain with a terminal double bond. (**Figure 3**). The competitive of recombination reaction and disproportionate reactions between growing polymer macroradical and nitroxide is crucial to achieve a good control in NMRP. Depending on the employed nitroxide and kind of polymerization system, these two competitive reactions can occur with various rate.
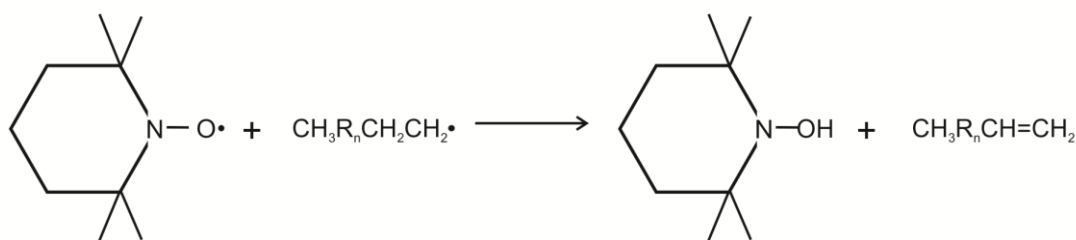
Figure 3. The scheme of disproportionate reaction occurring between TEMPO radical and growing polymer macroradical.

The description of the publications

I.   **The design of novel unimolecular initiators for NMRP (the publications: H1, H2, H4).**

In the design of novel unimolecular initiators for NMRP the following three reactions should be mainly considered: the homolytic decomposition of alkoxyamine under influence of heat or light, the recombination reaction occurring between growing polymer macroradical and nitroxide and disproportionation process which is competitive to the recombination. The properly designed unimolecular initiator should

be able to easily decompose, the nitroxyl radical generated in this process should easily recombine with growing polymer macroradical and simultaneously should participate insignificantly in disproportionate reaction.

My research, concerning the design of novel unimolecular initiators for NMRP, focused on the derivatives of TEMPO radical. This nitroxide was successfully applied in the polymerization of styrene and its derivatives. The polymers with narrow polydispersity and well chain-end functionality were prepared in such a manner.[5] However, in the case of some vinyl polar monomers such as methyl acrylate, ethyl acrylate, vinyl acetate, acrylonitrile, the polymerization process cannot be well controlled, using TEMPO as mediator, under the conditions used for homopolymerization of styrene.[6] Some copolymerization systems consisting acrylates or acrylonitrile with styrene were performed in controlled fashion by using TEMPO but only when styrene concentration in the feed was not to low (mole fraction of styrene in feed was greater than 0.5).[6]

Hua et al. reported the kinetics of copolymerization styrene with acrylonitrile controlled by using TEMPOL (**2**). They showed that the consuming rate and conversion of acrylonitrile in copolymerization system were significantly lower than those determined for styrene. Authors proposed that the process of disproportionation of growing macroradicals ended with acrylonitrile unit occurs faster than these ones ended with styrene unit. Thus, the radicals ended with the acrylonitrile unit are unable to propagate with acrylonitrile molecule. As a consequence a larger amount of styrene in a mixture with acrylonitrile is necessary for a successful control over polymerization process.[7]

Analyzing the results reported by Hua et al.[7] I wondered whether only kinetic effect of disproportionate reaction is responsible for unsuccessful control over polymerization in styrene/acrylonitrile/TEMPO system. I decided to analyze the C-ON bond strength for several N-alkoxyamines which can be considered as models for dormant forms of propagating chains in the copolymerization process of styrene with acrylonitrile in the presence of TEMPO. The terminal and penultimate models were taken into consideration. I determined homolytic bond dissociation enthalpy (BDE) of the C-ON bond, for several N-alkoxyamines derived from TEMPO, on the basis of quantum-mechanical calculations. The knowledge of BDE values for the investigated adducts gave some explanations concerning the mechanism and difficulties in copolymerization of acrylonitrile in controlled fashion.

The detailed analysis of the factors influencing the C-ON bond strength turned out to be helpful in the design of new effective unimolecular initiators NMRP in further steps of my research.

The chemical structures of the investigated N-alkoxyamines are presented in **Figure 4 (publication H1).**
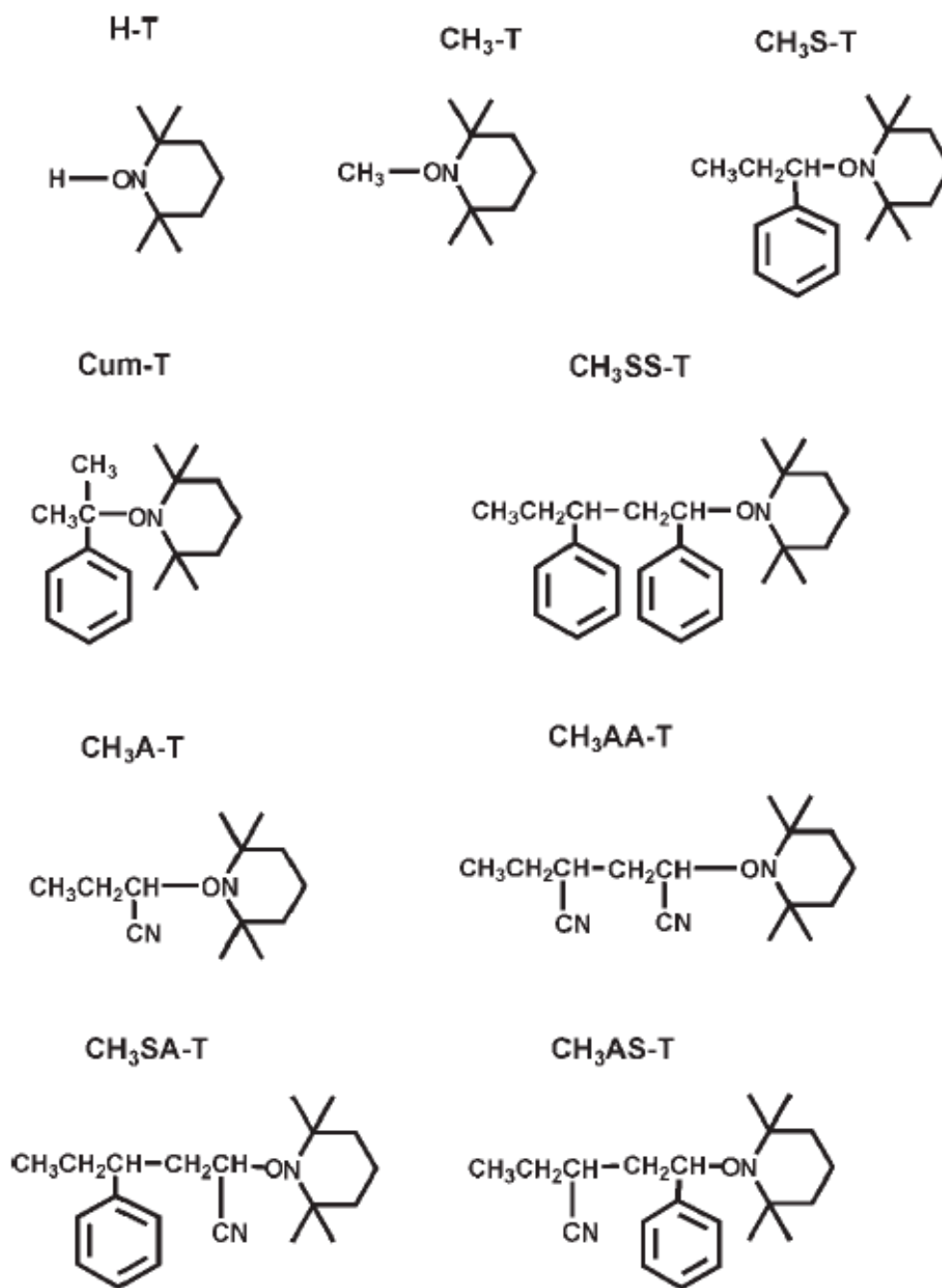
Figure 4. The structures of investigated N-alkoxyamines (publication **H1**).

The molecules **CH₃S-T** and **CH₃A-T** have been adopted as models of dormant forms according to the terminal model, whereas the N-alkoxyamines **CH₃SS-T** i **CH₃AS-T, CH₃SA-T** and **CH₃AA-T** as the adducts according to penultimate model.

To verify my calculations, the BDE values were calculated for molecules similar to the investigated compounds for which the experimental and theoretical data are available in literature (**H-T, CH₃-T**, **Cum-T**).

The results presented in publication **H1** were obtained using the computational resources of the Interdisciplinary Center for Mathematical and Computational Modeling at Warsaw University with the Gaussian 03 software package.

The BDE values determined at four levels of theory are presented in **Table 1.** Three among them were performed using density functional theory (DFT) with Becke functional and functional correlations given by Lee (B3LYP) in various standard basis set. Additionally, the integrated method (IMOMO) were used for the molecules corresponding to the dormant forms in terminal model. IMOMO combines a high level *ab initio* correlated calculation for small model subsystem with the molecular mechanics for a large real system. Besides that, the homolytic dissociation enthalpy of hydrogen atom (BDH) was also calculated (at the same levels of theory) in the molecules created by replacement of TEMPO molecule with the hydrogen atom. It has allowed me to compare stability of the radicals formed during homolysis of the relevant N-alkoxyamines. As the correlation between BDE and BDH can be taken as a rough measure of stabilization effect on the BDE for leaving radical.

Table 1

BDE(C-ON) values of investigated N-alkoxyamines (**Figure 4**) and BDH of molecules created by replacement of TEMPO radical in these molecules with hydrogen atom.

| | DFT/B3-LYP/ | | | | Literature | |
	6-31G(d)	6-311G++ (2df,p)	6-311+G (3df,2p)	IMOMO G3:ROMP2/ 6-31G(d)/B3LYP/6-31G(d)	Experimental	Theoretical
BDE (kcal/mol)						
H-T	59.7	61.4	63.2	68.0	69.7[a], 69.6[b]	66.6[e]
Cum-T	19.5	13.7	13.7	29.2	24.6[c], 26.2[d]	21.3[e], 25.1[f]
CH_3-T	42.0	37.0	38.4	47.0	47.1[e]	44.1[e], 42.5[f]
CH_3S-T	24.3	18.3	19.7	32.3		
CH_3A-T	23.7	18.6	19.7	25.9		
CH_3SS-T	16.7	10.7	12.2			
CH_3AA-T	23.8	18.4	19.7			
CH_3SA-T	24.2	19.0	20.2			
CH_3AS-T	22.6	16.3	17.7			
BDH (kcal/mol)						
Cum-H	82.3		80.3	82.2	84[b]	
CH_3-H	102.7		100.7	102.0	104.8 ± 0.1[a]	102.9[a]
CH_3S-H	84.4		82.1	88.5		
CH_3A-H	87.7		86.0	88.4		
CH_3SS-H	79.8		77.8			
CH_3AA-H	86.6		84.8			
CH_3SA-H	87.7		85.8			
CH_3AS-H	85.0		82.7			

[a] Obtained from measurements in solution from semiempirical equation based on a thermodynamic cycle.[91]
[b] Determined by a direct calorimetric technique in solution.[92]
[c] Bond dissociation energy (not enthalpy),[93] estimated from data by Ingold et al.[94,95]
[d] Ref. 96.
[e] Calculated with B3P86/6-31G(d)//HF/6-31G(d).[47]
[f] Calculated with semiempirical method PM3.[25]

For alkoxyamines **CH_3S-T** and **CH_3A-T BDE** values of BDE are equal; however the significant differences are for the molecules **CH_3SS-T** and **CH_3AS-T, CH_3SA-T** and **CH_3AA-T**. The values of BDE for these molecules decrease as follows **CH_3SA-T >**

CH₃AA-T > CH₃AS-T > CH₃SS-T, wherein the difference between BDE value for the **CH₃SA-T** and **CH₃SS-T** is up 7.5 kcal/mol.[a] It means that the styrene unit, located in penultimate position, influences on stability of C-ON bond. Thus, the addition of the next molecule of monomer requires more energy (in order to decompose C-ON bond) in the case of acrylonitrile as the terminal unit than in the case of styrene. The presence of two alongside styrene units in the propagating chain dramatically weakened the C-ON bond in TEMPO-derived alkoxyamine. For **CH₃SS-T** alkoxyamine BDE is smaller by ~ 30% when compared with the remaining alkoxyamines. It was demonstrated that log k_d (where k_d is the experimental determined hemolytic dissociation rate constant) is directly proportional to the calculated BDE values,[8] so the observed differences should also correspond to kinetic effects. Notably, that the publication **H1** was the first which reported existence of penultimate unit effect on stability of C-ON bonds in the styrene/acrylonitrile/TEMPO polymerization system.

The publication **H1** also presents detailed analysis of polar, steric and stabilization effects on C-ON bonds homolysis. A thorough analysis of the studied alkoxyamines structures led me to the conclusion that the strength of C-ON bonds depends primarily on steric and electron delocalization effects.

Additionally, the presence of substituents inducing much greater electron delocalization in alkoxyamine molecule should decrease the stability of C-ON bond and consequently favors the initiation in polymerization system.

In the next step I studied the influence of the presence of carbonyl group in alkoxyamine on stability of C-ON bond. According to my hypothesis, due to the polar and delocalization effects of carbonyl group, the stability of radical generated as a result of alkoxyamine homolysis should be greater therefore the BDE values should be lower and rate constants of homolysis k_d should be higher. Consequently, the polymerization process using such an alkoxyamine could be initiated at lower temperature compared with previously studied.

The results of quantum-mechanical calculations of BDE(C-ON), performed for several alkoxyamines functionalized carbonyl group, confirmed my hypothesis. The presence of the ketone group in the alkyl fragment of alkoxyamine (**Figure 5**, structure **C3a**) causes that the value of BDE is significantly decreased. For **C3a** the determined BDE (at BMK/6-311+G(3df,2p) level of theory) was by 22 kJ/mol lower compared with unfunctionalized alkoxyamine (**Figure 5**, structure **C2a**).

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[a] determined at B3LYP/6-31G(d) level of theory (the results from others levels were similar).
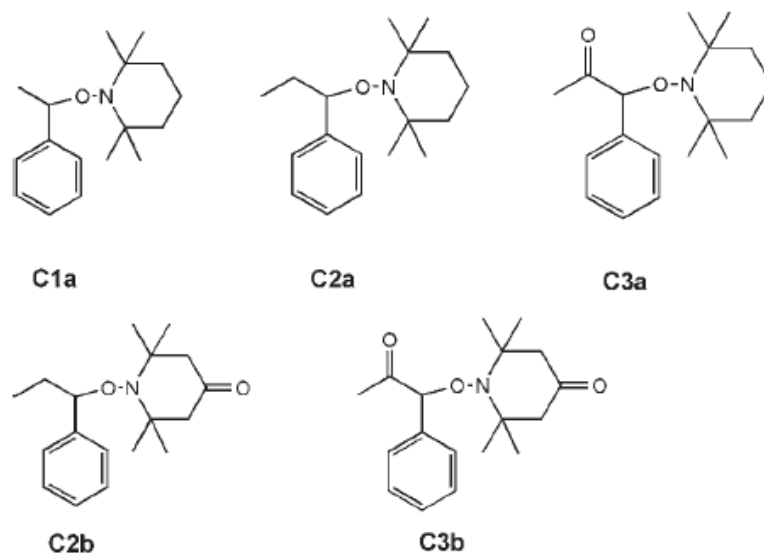
Figure 5. The structures of the investigated N-alkoxyamines (publication **H2**).

Since the results of theoretical studies were such a promising I decided to develop synthesis and perform an experimental kinetic studies for the compounds which were a subject of theoretical studies. For **C1a, C2a, C3a, C2b, C3b** (**Figure 5**) I determined the rate constants of the C-ON bond homolysis and thermodynamic activation parameters for bond homolysis (enthalpy of activation, entropy of activation and free energy of activation). The rate constant of homolysis (k_d) determined for alkoxyamine functionalized with ketone group in β position (structure **C3a**) turned out almost 500 times higher (at temperature of 363°K) compared with that for unfunctionalized alkoxyamine (structure **C2a**). The performed analyses of frontal orbitals and spin distribution allowed me to indicate that the decrease in the strength of C-ON bonds in ketone functionalized alkoxyamines in the alkyl fragment predominantly originates from a substantially smaller HOMO-LUMO gap and more delocalized spin density in leaving alkyl radicals compared with unfunctionalized alkoxyamines.

Next, the ketone functionalized N-alkoxyamine **C3b** has been applied as a new unimolecular initiator in the preparation of (α, ω) functionalized (telechelic) polymers. (**Figure 6**).
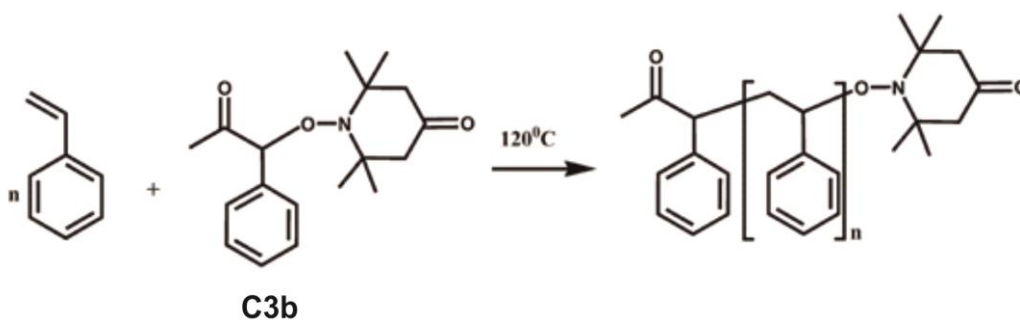

Figure 6. The scheme of synthesis of telechelic polystyrenes using **C3b** as unimolecular initiator (publication **H4).**

The compound **C3b** was successfully used as unimolecular initiator for NMRP. The polymerizations in the presence of **C3b** were well controlled, the obtained molecular weight distributions of polymers were narrow, polydispersity indexes below 1.3 and degree of functionalization above 1.

In **Table 2** the times of polymerizations and selected results from SEC analyses (Size Exclusion Chromatography), monomer conversions and degree of functionalization are presented.

Table 2
Time of polymerization (t), number-average molecular weight (M_n) and weight-average molecular weight (M_w), polydispersity indexes (PDI=M_w/M_n), percent of monomer conversion (% Conv), average number of C=O group for the one polymer chain from UV-Vis measurements (DF). The polymers P1-P5 were obtained without addition of Acetic Anhydride (AA) as accelarator, PA denoted the polymers obtained with addition of AA.

Polystyrene	t (h)	$\bar{M}_n \times 10^3$ (Da)	$\bar{M}_w \times 10^3$ (Da)	PDI	% Conv.	DF
P1	1	4.51	5.65	1.15	7.60	1.98
P2	3	5.86	6.79	1.16	21.6	1.50
P3	4	11.8	15.0	1.20	32.9	1.40
P4	24	16.8	20.3	1.20	80.9	1.20
P5	24.5	19.1	23.0	1.22	91.9	1.20
PA2	2	9.22	15.8	1.46	32.1	0.59
PA4	4	16.1	23.5	1.71	60.3	0.18

The results reveal that the molecular weight distribution is very narrow for the short time of polymerization (P1 and P2), while if the time of polymerization is longer, the weight distribution broadens on the side of high molecular weights (**Figure 7).** To achieve a high conversion of monomer, long time of polymerization was required (80% after 24 h). The addition of acetic anhydride (AA) during the polymerization results in significant acceleration of the polymerization rate (PA2, PA4).

The presence of the ketone groups in polymer chains was confirmed by the synthesis of hydrazons by means of 2,4-Dinitrophenylhydrazone (DNPH). Quantitative analysis of the functionalized derivatives was performed by measuring the absorptivity of the hydrazone of polymers and the hydrazone of the initiator. The determined degrees of functionalization (defined as an average number of C=O group for the one polymer chain denoted DF) are presented in **Table 2**. For lower conversions (below 20%) DF values are close to theoretical predictable value 2 and exceed 1 per one polymer chain for all other samples.

The addition of AA to the polymerization system increased the conversion from 5% to 13%/h. However, molecular weight distribution for polymers obtained after the addition of AA was significantly broader and polydispersity indexes above 1.5 (**Table 2**). The degrees of polymers functionalization obtained using AA were below 1 (**Table**

2). Hence, the polymerization of styrene in the presence of AA was controlled with a lower degree.

It is worth pointing out that the polymerizations of styrene initiated by using the developed compound **C3b** met all requirements for well-controlled process e.g. 1) linear relashionship between conversion and time, 2) linear relationship between ln(1/1-Conv) and time (indicates that the polymerization process follows the first-order kinetics with respect to the monomer and the radical concentration remains constant), 3) low polydispersity indexes (PDI<1.5), 4) linear dependence of molecular weight on conversion, 5) quantitative functionalization of polymer chains, 6) possibility of further propagation of polymer chains after addition of another portion of (co)monomer.[5]
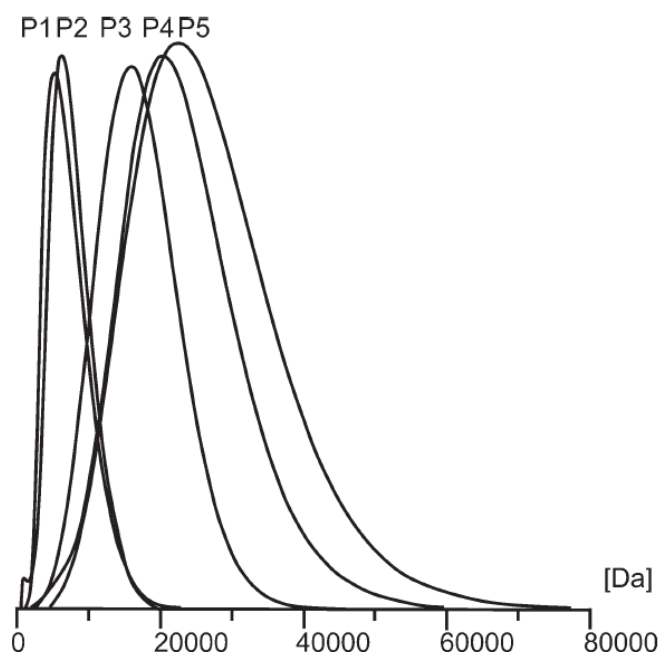

Figure 7. The weight distribution curves for polymerization of styrene with **C3b** as unimolecular initiator (molar ratio M:I=300:1). Time of polymerization and % of conversion are shown in **Table 2**.

The obtained telechelic polymers are of great importance in the synthesis of new biohybrid materials such as bioconjugates with proteins or peptides as well as new polymer nanostructures for medical applications. Due to the presence of the ketone groups they can easily react with compounds containing amine groups (for instance through reductive amination).

II.   Surface modification of nanomaterials using nitroxides (papers H3, H5, H7, H9)

The design and fabrication of modified surfaces is a pivotal research issue in modern materials science. Appropriate surface modification is an effective approach in the

preparation of new tailor-made materials for catalytic, protective, biomedical, sensory and many other purposes.

The processes toward modification of nanomaterials surface have attracted much interests in the recent years. The nanomaterials exhibit the unique physical and chemical properties. Among them are nanoparticles (diameter size in the range of several to 100 nm), nanoclusters (diameter size < 2 nm), nanotubes (diameter <100 nm, length few μm), fullerenes and quantum dots.[9] Surface modification of nanomaterials provides them many useful properties such as the following: 1) inherent stability against aggregation, 2) diverse functionality, 3) solubility or dispersibility in appropriate solvents and polymer matrices, 4) ability to self-assemble and others.[10]

Although TEMPO and many of its derivatives are known from the 1960s; however the first reports on their use in surface modification processes appeared just twenty years ago. Until now, silica and silicon flat surfaces, magnetic particles (cobalt and Fe_3O_4), gold, silver nanoparticles, many different polymers, carbon nanomaterials such as nanotubes, fullerenes and graphene as well as graphene oxide have been successfully grafted with TEMPO.

My original papers on modification of nanomaterials' surface with nitroxides concern gold and silver nanoparticles.

Gold nanoparticles (AuNPs) are the most stable metal nanoparticles and they are extensively studied due to their fascinating quantum-size-related electronic properties as well as unique biological and catalytic activity. The properties of AuNPs strongly depend on their size, shape and kind of stabilizing ligand.[11] It was demonstrated that AuNPs can be successfully applied in catalysis (pseudo-homogenic and recyclable catalysts),[12] nanomedicine (vectors for drugs and genes delivery and contrast agents in cancer diagnosis),[13] optoelectronics (ultra-fast optical switches and ultra-sensitive (bio)sensors).[11]

AuNPs functionalized with nitroxides (N-AuNPs), also called spin labeled nanoparticles, are especially interesting due to their paramagnetic properties. Hence N-AuNPs can find many further important applications such as a novel spin probes in biochemical studies as well as new materials for cancer diagnosis/therapy and fabrication of spintronic devices.[14] For all these purposes the grafting density of nitroxides attached to the nanoparticle must be sufficiently high. To this end, I proposed the method based on chemisorption of ligand DiSS (bisnitroxide disulfide) onto gold nanoparticles closed in reverse micelles of tetraoctylammonium bromide (TOBA).

DiSS
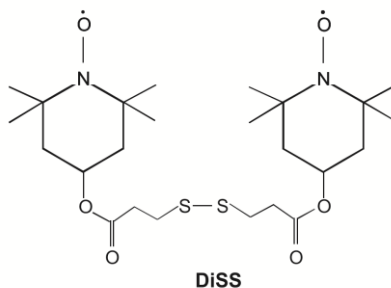
In contrast to the method proposed earlier by Chechik and co-workers[15] for the synthesis of N-AuNPs, the method proposed by me is one-step and thanks to that allows to obtain the nanoparticles with higher grafting density. Precisely, due to the elimination of the ligand exchange reaction with AuNPs protected by thiols higher nitroxide coverage can be achieved. Spin-labelled AuNPs, obtained according to the developed protocol, have a multilayer structure consisting of covalently attached nitroxyl ligands and weakly adsorbed tetraoctylammonium bromide ion pairs.
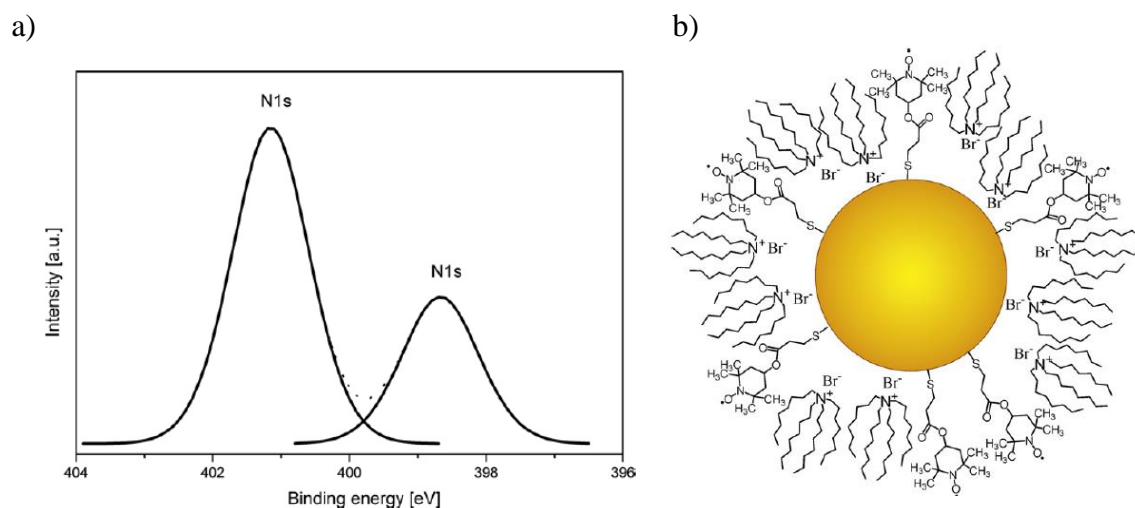
a)   b)

Figure 8. a) Partial XPS spectrum of AuNPs showing two peaks with the binding energies of 398.7 eV and 401.1 eV corresponding to N1s electrons from the nitroxyl group and the tetraoctylammonium ion, respectively. b) The proposed structure of the obtained nanoparticles (publication **H3**).

X-ray photoelectron spectroscopy (XPS) showed the presence of gold, sulfur, nitrogen, oxygen, carbon and bromine atoms in the synthesized material. Binding energies obtained from the XPS spectrum excellently confirmed the presence of two types of ligands: non-covalently attached tetraoctylammonium ions and TEMPO derivatives covalently attached to Au *via* thiolate bonds (**Figure 8a**). AuNPs prepared according to procedure described in publication **H3** have narrow size distribution (1.90±0,54 nm), are stabilized by two types of ligands (**Figure 8b**) and they are soluble in both polar and non-polar organic solvents.

A further step in my research was the preparation of gold nanoparticles with average diameter ca. 2.5 nm coated only with nitroxyl ligands by one-phase procedure, using DiSS as a stabilizing agent. The obtained nitroxide coated gold nanoparticles (N-AuNPs) were immobilized on the gold electrode surface by means of a 1,9-nonanedithiol linker. This electrode was applied in electrocatalytic oxidation of benzyl alcohol to benzyl aldehyde. The catalytic efficiency of the N- AuNPs nanostructured gold electrode was compared with that of a self-assembled monolayer of nitroxides formed *via* direct chemisorption of DiSS on the gold surface (**Figure 9**).
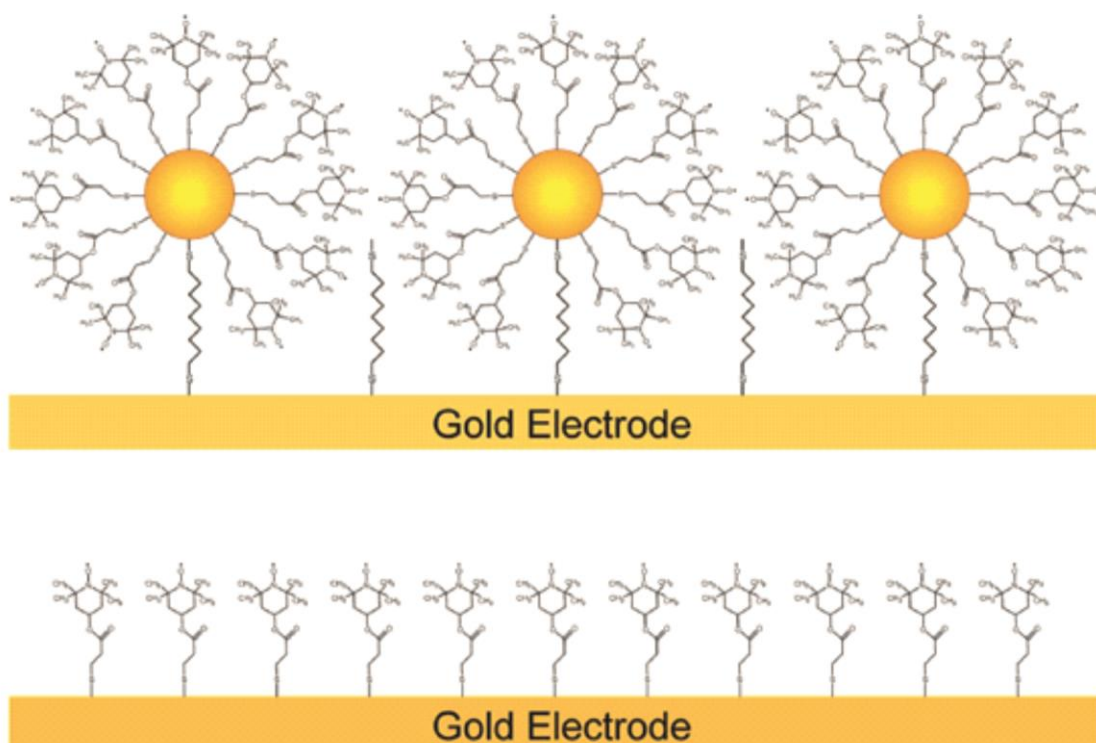
Figure 9. The scheme of an electrode modified with N-AuNPs obtained using DiSS as a stabilizing agent (above) and an electrode modified with monolayer obtained *via* direct chemisorption of DiSS on a flat gold surface (below). Reported in the publication **H5.**

The results presented in publication **H5** showed that the electrocatalytic oxidation of benzyl alcohol is more efficient on the electrode nanostructured modified with N-AuNPs compared to the electrode modified with DiSS *via* direct chemisorption on a flat gold surface. Our results also showed that an electrode modified with N-AuNPs can be successfully applied as a new type of catalyst for selective alcohol oxidation that can be easily removed from the reaction medium and reused.

Recently our research group was the first to apply TEMPO derivatives in the surface modification of silver nanoparticles (AgNPs). Due to the bioactivity of AgNPs and nitroxides the preparation of the material which combines them seemed to be extremely promising for potential biomedical applications.

I developed one-phase and one-step procedure for the preparation isolatable, devoid of Ag$^+$ impurities, long-term stable, spherical nitroxide-coated silver nanoparticles with an average diameter ca. 7 nm and high grafting density of TEMPO moieties on the surface (7 TEMPO moieties/nm^2). As it turned out the prepared nitroxide-coated silver nanoparticles (N-AgNPs) exhibited high antibacterial activity toward both Gram-negative and Gram-positive bacteria strains.

Figure 10 shows the scheme of the procedure for the preparation of N-AgNPs (reported in the publication **H7)** and two proposed for N-AgNPs structures.
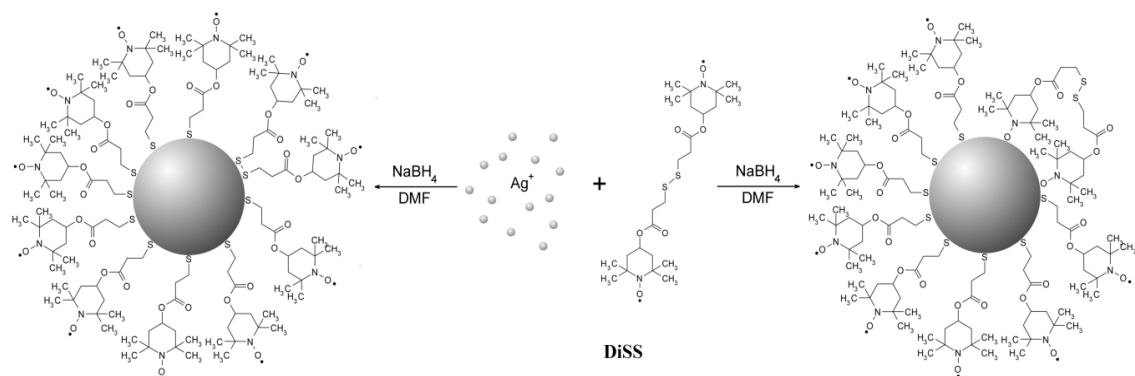

Figure 10. The synthetic route and two proposed structures of nitroxide-coated silver nanoparticles (N-AgNPs). (publication **H7**).

For the prepared nanomaterials, precise broth microdilution assays have been performed using several Gram-negative bacteria i.e. *Escherichia coli, Pseudomonas aeruginosa*, *Klebsiella pneumonia* and Gram-positive bacteria i.e. *Staphyloccocus aures*, *Staphyloccocus epidermis* (mostly pathogens). The obtained results are presented in **Table 3**. Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) values were determined on the basis of three separate experiments.

Table 3

MIC and MBC values of N-AgNPs.[a] Results of three separate experiments are presented; no differences were noticed among experiments.

Bacterial strain	MIC and MBC[b] [$\mu g\ ml^{-1}$]				
	AI24RT	AI24RTH	AI2HH(+5)	AI2HH(−5)	AR2HH(−5)
E. coli ATCC 23546	32	64	12	8	8
P. aeruginosa ATCC 10145	16	16	8	4	4
K. pneumoniae ATCC 13886	12	12	8	4	4
S. aureus ATCC 29213	32	64	12	12	12
S. epidermidis ATCC 12228	16	24	4	4	4

[a] Contents of silver in the studied materials are given in Fig. 9. [b] Solution of the highest used concentration of DMSO (4% v/v) and DiSS (128 μg ml^{-1}) were used as the control samples and they do not affect the normal growth of bacteria.

In the case of nanoparticles obtained under the optimal conditions (AR2HH(-5)) the values of MIC oraz MBC are very low (toward Gram-negative below 10 ppm, toward Gram-positive slightly higher but below 15 ppm). The determined MICs and MBCs values are significantly lower than those reported in literature for thiolate-capped AgNPs with similar size and polydispersity. So, the results reported in publication **H7** indicate that the nitroxide coverage of silver nanoparticles favours their antibacterial

activity. I proposed in the publication **H7** possible explanation of this fact. It is most likely that the nitroxides covering silver surface may be oxidized under influence of Reactive Oxygen Species (ROS) to positively charged oxoammonium ions, which are capable of strong interactions with negatively charged bacterial membrane leading to its physical damage and probably chemical modifications.

The synthesized N-AgNPs have been characterized using transmission electron microscopy (TEM), several spectroscopic methods (FTIR, EPR, UV-vis, XPS) and thermogravimetric analysis (TG). FTIR and XPS confirmed functionalization of silver surface with nitroxide used in the synthesis and showed the presence of intact disulphide bonds in organic layer. On the basis of the EPR spectra simulations and quantitative data from XPS analysis I estimated that *ca.* 8% of ligands (biradicals) are attached by disulphide groups adsorbed on the surface, *ca.* 90% of ligands is attached to the silver surface as thiolate moieties and *ca.* 1-2% are linked *via* Ag-O bonds that involve unpaired electrons of nitroxides and conduction electrons from silver surface (see **Figure 10).** The comparison of the results reported in publication **H5** with reported in publication **H7** allowed me to show that the mechanism of chemisorption of bis-nitroxide disulfide on the silver surface differs from that on a gold surface.

My publication **H9** presents an overview of the methods for surface modification based on the use of TEMPO and its derivatives (reported in literature until July of 2017). The presented methods can be divided into two groups: 1) the first relies on the immobilization of TEMPO moieties on the surface of various materials (with easily available nitroxyl moieties) (**Figure 11a**), 2) the second utilizes TEMPO and its derivatives for the grafting of polymer chains and polymer brushes formation on flat and nanostructure surfaces *via* NMRP (**Figure 11b**).
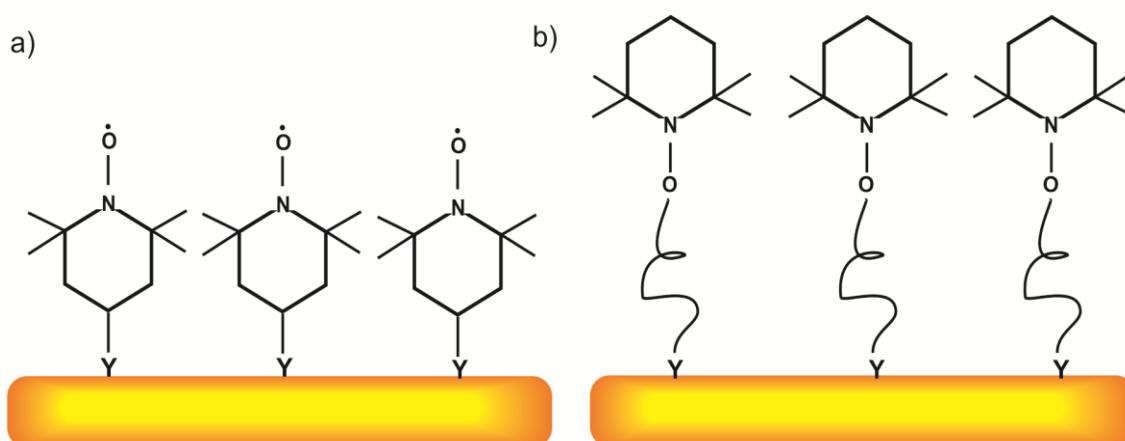

Figure 11. Two discussed in the publication **H9** approaches to surface modification using TEMPO and its derivatives: with easily available nitroxyl groups a), and nitroxyl groups connected with polymer chains b). The linker molecule connecting directly with the surface was denoted Y.

The publications **H3**, **H5** i **H7** concern immobilization of TEMPO moieties on the surface of nanomaterials, while the publications **H6** i **H8** report the formation of polymer brushes on nanostructure surfaces using TEMPOL (**2**) as mediator. The publication **H9** shows results of my research described in the publication **H3, H5, H6, H7 i H8** in comparison with the methods reported in literature.

III. Application of nanoparticles coated with nitroxides in the preparation of functional polymer materials using NMRP (the publications: H6, H8, H9).

Surface grafting with polymers consists of covalent attachment of polymer chains to a chemically active surface. Grafting of polymers is also called polymer brush formation but only in cases where grafting density achieved is high enough to force polymer chains to stretch away from the surface. There are two main strategies for surface modification with polymers attached *via* covalent bonds: the (1) "grafting to" approach based on the reaction of end-functionalized polymers with the surface and (2) "grafting from" approach consisting of surface initiated polymerization wherein the polymerization initiator is immobilized on the surface of the substrate from which the polymer chains grow *in situ*. However, "grafting to" approach is limited to preaparation of relatively low density polymer shells.[16]

As a result of "grafting" to/from surface of nanoparticles, the hybrid nanostructures with core/shell architecture can be obtained. These nanohybrids combine unique properties of nanoparticles with useful characteristic of polymers. Additionally, the surface modification of nanoparticles with polymers provides them many beneficial properties that are crucial for their wide applicability. Among other properties, it significantly increases the stability and dispersibility of the nanoparticles in organic solvents as well as within polymer matrices. [16]

In the publication **H6** a facile and novel route to synthesis of core/shell nanohybrids, based on application of TEMPO covered gold nanoparticles (T-AuNPs), have been proposed. The developed procedure consists on late injection of T-AuNPs into a TEMPOL (**2**) mediated styrene polymerization system and continuing of the polymerization for 2h, 4h or 6h (**Figure 12**). T-AuNPs have been synthesized according procedure reported in the publication **H5** (with slight modifications).

Figure 12. Synthetic route to the preparation of hybrids with nanogold core and polystyrene shell (AuPS). (reported in the publication **H6**).

I hypothesized that after the introducing of T-AuNPs into polymerization system, the polymer macroradicals created as a result of homolysis C-ON bonds can recombine with TEMPO radicals attached to nanoparticle surface. Simultaneously, during further polymerization the attached polymer chains can be reversibly detached from the surface and propagate but the propagation will proceed slowly because the presence of TEMPOL (**2**) in polymerization system. The hypotheses have been fully confirmed by performed experimental studies. SEC analyses showed that both the hybrid nanostructures and the polymers attached to the nanoparticles characterize narrow polydispersity (PDI<1.3).

The mechanism of grafting polymer chains on nanoparticles surface through radicals recombination has been confirmed using EPR spectroscopy. **Figure 13** shows EPR spectra recorded for T-AuNPs and core/shell nanostructures obtained according to scheme illustrated in **Figure12**. As can be seen, EPR signal completely disappears for AuPS nanostructures.
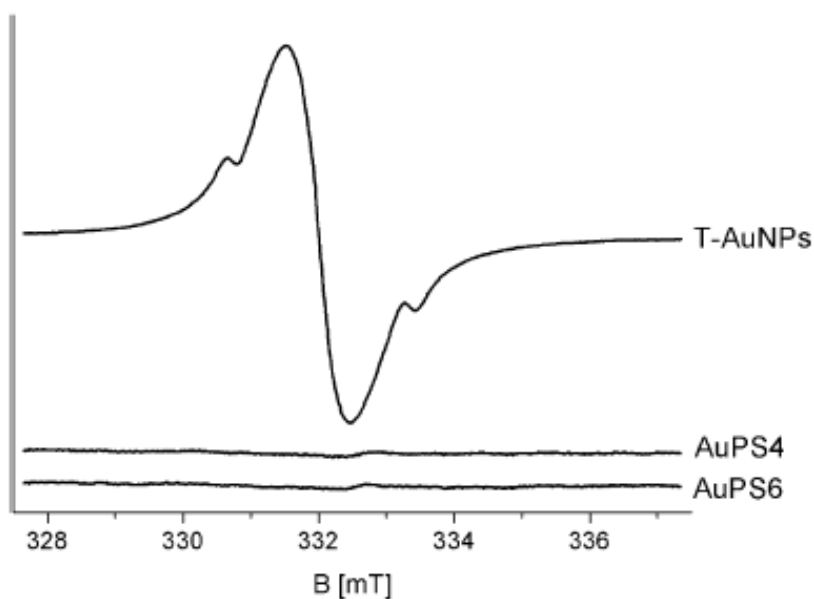
Figure 13. EPR spectra of T-AuNPs (in acetone solution) and polystyrene coated nanoparticles AuPS (in THF solution).

TG analyses in connection with UV-vis spectroscopy revealed that the polystyrene coating on the gold nanoparticles surface significantly improves their thermal stability. T-AuNPs are stable below $160^{o}C$ (in solid state, under helium atmosphere). The polymer coating efficiently protects nanoparticles against aggregation even at $300^{o}C$. Furthermore, the thermal stability of the obtained nanohybrids is slightly higher than the thermal stability of pure polystyrene. Simultaneously, the obtained nanomaterials exhibit surface plasmon resonance (SPR) observed near 520 nm that provides an opportunity to apply them as high-temperature optical sensors.

The developed procedure (reported in the publication **H6)** allowed to obtain a hybrid nanostructures with nanogold cores and precisely designed polystyrene shells. TEM analyses showed, that the size and shape of gold nanoparticles do not change during polymerization. On the other hand, thickness of polymer shell can be easy designed using appropriate molar ratio monomer:initiator:TEMPO or proper time of preliminary polymerization before or after of T-AuNPs injection.

Next, the procedure for synthesis of hybrid nanostructures (reported in the publication **H6**) was applied by me in the preparation of polystyrene grafted silver nanoparticles. Because gold and silver nanoparticles functionalized with TEMPO differ in their properties the procedure used in the case of T-AuNPs had to be modified for T-AgNPs. This modified procedure (described in the publication **H8)** allowed to fabricate polystyrene grafted silver nanoparticles (Ag@PS) with exceptionally high grafting density, even a hundred-fold higher than the grafting densities reported so far. Such a high grafting density was possible because the nitroxide radicals attached to the silver surface are capable of recombining with polymer macroradicals and therefore

form covalent bonds. Importantly, thanks to the appropriate length of the linker the steric effects during the grafting process can be significantly limited. Due to the high flexibility of polymer chains attached to the silver surface through a nitroxide linker, the free volume effect enables interpenetration of polystyrene molecules, providing excellent mutual miscibility of Ag@PS with the polymer matrix **(Figure 14).** As it turned out, the synthesized nanohybrids **(Ag@PS)** and their nanocomposites **(PS/Ag@PS)** exhibited effective antibacterial activity against pathogenic bacteria: *Pseudomonas aeruginosa* (Gram-negative representative) and *Staphylococcus aureus* (Gram-positive representative).
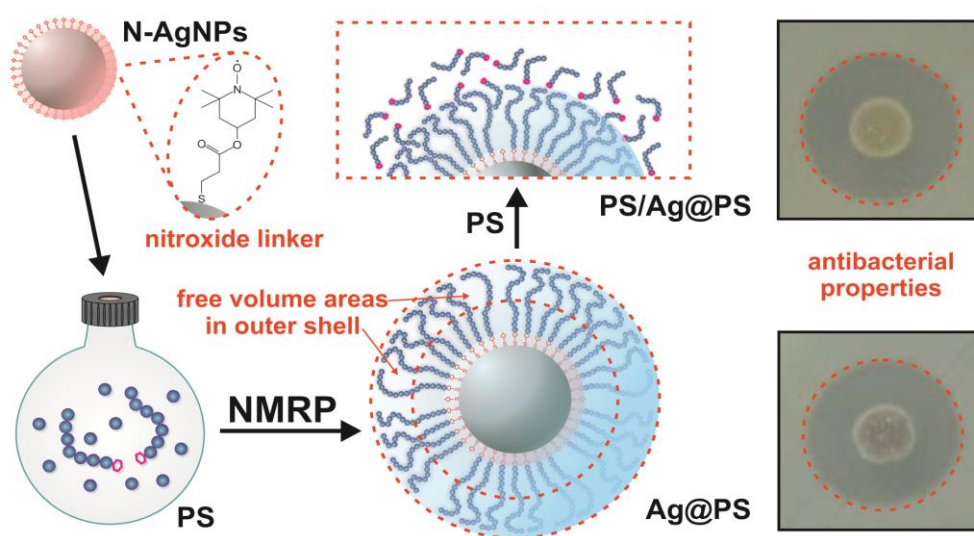

Figure 14. The scheme for the preparation of polystyrene grafted silver nanoparticles **(Ag@PS)** and their nanocomposites **(PS/Ag@PS)** proposed in the publication **H8.** The selected pictures of microbiological tests are also presented.

It is worth noting that the developed procedure for the preparation of Ag@PS PS/Ag@PS is a subject of patent application which was submitted to Urząd Patentowy RP. My co-authors in this patent application are Piotr Krystosiak and Katarzyna Markowska. Piotr Krystosiak worked with me on the invention development within his BSc and MSc studies under my supervision, Katarzyna Markowska was a PhD student at Faculty of Biology University of Warsaw and she performed microbiological measurements.

Notably, the procedure for the fabrication of polystyrene grafted silver nanoparticles proposed earlier by Greiner[17] and co-workers was based on the application of living anionic polymerization in "grafting to" approach. In the publication **H8** we first reported successful application of NMRP to the preparation of such type of nanomaterials. In comparison with living anionic polymerization, NMRP does not require rigorous conditions (i.e. ultra pure and utra dry reagents, specialized glassware). Thus, NRMP is a powerful alternative to anionic polymerization giving chance for utilization of the developed procedure on a scale larger than laboratory.

In the publication **H8** we also report detailed characteristic of the prepared nanomaterials (nanohybrids and their nanocomposites) by using microscopic (TEM), spectroscopic (EPR, UV-vis), thermogravimetric (TG) and dynamic light scattering (DLS) methods. Furthermore, three independent assays showed that the synthesized nanohybrids and their nanocomposites exhibit effective antibacterial activity against both Gram-negative (*P. aeruginosa*) and Gram-positive (*S. aureus*) pathogenic bacteria.

Due to the easy processability, high thermal stability, and simultaneously effective antibacterial activity, the fabricated nanocomposites are highly promising antibacterial materials for a variety of biomedical applications such as preparation of medical equipment coatings, manufacturing of surgical instruments, dental tools, dressing materials, and prosthesis.

In review paper **H9**, the methods for the grafting of polymers using TEMPO and its derivatives reported in literature until July 2017 are presented. The paper **H9** provides an overview of the methods for the grafting of polymer chains and toward the polymer brushes formation both on flat and nanostructure surfaces (nanoparticles, fullerenes, carbon nanotubes, graphene, graphene oxide). A critical review of the reported methods and their comparison with the methods proposed by me in the publications **H6** and **H8** have been presented there. A comparative analysis showed that the polymer brushes formed according to the procedures described in the publications **H6** and **H8** have significantly higher (even a hundred-fold higher) grafting densities than the densities reported so far. Importantly, the structure of (co)polymers attached to the surface of nanoparticles can be precisely designed.

Summary

In this dissertation I presented the series of thematically interconnected publications, constituting the scientific achievement, which includes 8 of original papers and 1 review paper. The achievements reported in these publications are my contribution to the development of polymer chemistry, materials chemistry and nanotechnology.
I consider my major achievements to be as follows:

- showing that the steric and delocalization effects mainly decide about stability of C-ON bond between TEMPO and growing macroradicals in styrene-acrylonitrile polymerization system mediated by TEMPO,
- demonstrating that the penultimate unit effect influences on stability of C-ON bonds in the styrene/acrylonitrile/TEMPO polymerization system,
- designing and obtaining of new effective unimolecular initiators for NMRP, functionalized with ketone groups,
- explaining of possible reasons for decreasing C-ON bond stability in N-alkoxyamines functionalized with ketone group in β position based on the increased delocalization of spin density in the leaving alkyl radical and decreased HOMO-LUMO gap in comparison with unfunctionalized alkoxyamines,
- obtaining of ketone functionalized telechelic polystyrenes with narrow polydispersity, potentially useful for the preparation of biohybrid polymers,
- obtaining of stable gold nanoparticles with narrow size distribution densely coated with nitroxides using disulfide bisnitroxide as stablizing agent in one-step synthesis,
- elaborating of effective methods for the modification of gold and silver nanoparticles using disulfide derivative of TEMPO,
- proposing of the gold electrode modified with TEMPO coated gold nanoparticles as a novel, environmentally benign and recyclable catalyst for selective oxidation of alcohols to aldehydes,
- showing that the nitroxide coverage of silver nanoparticles favours their antibacterial activity against both Gram-negative and Gram-positive bacteria strains,
- explaining the increased antibacterial activity of silver nanoparticles covered by TEMPO by the effect of nitroxides oxidation under influence of Reactive Oxygen Species (ROS) generated on nanoparticle surface,
- showing that the disulfide bisnitroxides can be attached to the silver surface not only *via* Ag-S bonds but also through disulfide groups as well as *via* Ag-O bonds which involve unpaired electrons of nitroxides and conduction electrons from silver surface,

- elaborating of the method to fabricate thermoformable, perfectly homogeneous nanocomposites for medical applications using TEMPO-coated silver nanoparticles (patent application has been submitted to Urząd Patentowy RP),
- elaborating of the method to prepare hybrid nanostructures with core/shell architecture based on the recombination of nitroxides anchored to nanoparticles surface with polymer macroradicals generated in NMRP,
- elaborating of the method to fabricate hybrid nanomaterials with core/shell architecture and their nanocomposites for sensoric and medical applications.

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5. Other scientific publications and achievements

5.A Bibliographic summary of scientific achievements

Total number of publications: 22

Total numer of publications after PhD degree: 17

Total impact factor: $IF_{2016} = 57.502$

Citation report based on Web of Science at 9.10.2017:

Total number of citations: 129

Total number of citations (without self-citations): 111

Hirsch index: 7 (WoS); 9 (Google Scholar)

5.B The list of publications before receiving of the PhD degree in the journals listed in the Journal Citation Reports (except these listed in chapter 4)

[M1]. H. Wilczura, T. Kasprzycka-Guttman, E. Megiel," Heats of mixing of binary mixtures of pyridine bases and o-xylene.", Thermochim. Acta, (1994) 247, 237-243. IF= 2.18.

[M2]. T. Kasprzycka-Guttman, E. Megiel," Excess volumes of binary systems formed by 2,4,6-trimethylpyridine and n-alkane". Fluid Phase Equilibrium (1995) 113, 139-149. IF= 2.2.

[M3]. H. Wilczura, T. Kasprzycka-Guttman, E. Megiel,"Enthalpy of mixing for binaries: m-xylene + pyridine bases", Thermochimica Acta (1996) 274, 53-59. IF= 2.18.

[M4]. H. Wilczura-Wachnik, E. Megiel, T. Kasprzycka-Guttman,"Excess enthalpies for 4-methyltoluene + pyridine, + 2-methylpyridine, + 3-methylpyridine, + 4-methylpyridine, + 2,4-dimethylpyridine, + 2,6-dimethylpyridine, + 2,4,6 − trimethylpyridine at 298,15 K.", Journal of Chemical Engineering Data (1996) 41, 1514-1516. IF= 2.04.

[M5]. T. Kasprzycka-Guttman, H. Wilczura, E. Megiel, "Volumes of mixing 2,4-dimethylpyridine with n-alkanes.", Journal of Solution Chemistry (1996), 25, 1019-1028. IF= 1.2.

5.C The list of publications after receiving of the PhD degree in the journals listed in the Journal Citation Reports (except these listed in chapter 4)

[D1] E. Megiel, T. Kasprzycka – Guttman, A. Jagielska, L. Wróblewska, "A theoretical and experimental 14N NMR study of association of pyridine.", Journal of Molecular Structure (2001) 569, 111-119. IF= 1.60.

[D2]. E. Megiel, A. Kaim, "Molecular geometry and electronic structure of molecules in free-radical copolymerization of styrene and methyl methacrylate derived from density functional calculations" Journal of Polymer Science, Part A: Polymer Chemistry (2001) 39, 3761-3769. IF= 3.405.

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[D5]. A. Kaim, E. Megiel, "Transition Structures and Reaction Barriers in the Styrene - Acrylonitrile Copolymerization System According to Quantum Mechanical Calculations", Journal of Polymer Science Part A: Polymer Chemistry (2005) 43, 1827 - 1844. IF= 3.405.

[D6]. A. Kaim, E. Megiel, "Transition States for Deactivation Reaction in the Modeled 2,2,6,6-Tetramethyl-1-piperidinyloxy-Mediated Free-Radical Polymerization of Acrylonitrile." Journal of Polymer Science Part A.: Polymer Chemistry (2006) 44, 914 – 927. IF=3.405

5.D The list of publications after receiving of the PhD degree in the journals not listed in the Journal Citation Reports (except these listed in chapter 4)

[D7]. A. Kaim, E. Megiel, "Transition States For The Modeled Reactions of TEMPO with Hydrogen Atom." Indian Journal of Chemistry A-Inorganic Bio-inorganic Physical Theoretical & Analytical Chemistry (2009), 5,1-2. IF= 0.85.

[D8]. H. Sadegh, G. AM Ali, V- K. Gupta, A. Salam Hamdy Makhlouf, R. Shahryari-ghoshekandi, M. N Nadagouda, M. Sillanpää, E. Megiel, "The role of nanomaterials as effective adsorbents and their applications in wastewater treatment", Journal of Nanostructure in Chemistry, 2017, 1-14.

Elżbieta Megiel