

# Brochure of the International Workshop on Polymer Science and Polymeric Materials



**Bratislava • Budapest • Zabrze 2017**

## **EDITORIAL**

Brochure of the International Workshop on Polymer Science and Polymeric Materials published by Centre of Polymer and Carbon Materials Polish Academy of Sciences, Research Centre for Natural Sciences Hungarian Academy of Sciences and the Polymer Institute of the Slovak Academy of Sciences

The technical editors were Michał Kawalec, Joanna Rydz, Silvia Podhradská and Alena Šišková

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## CONTENT

Welcome to the International Workshop	3
Acknowledgement	4
Programme	5
 <i>Presentation of co-operating Institutions</i>	
Slovakia	6
Hungary	8
Poland	10
 <i>Workshop Contributions</i>	
Oral presentations	12
Poster presentations	18
 List of Participants	
BYPoS 2019, 8 <sup>th</sup> Young Polymer Scientists workshop	35
Notes	36
	37

## **WELCOME TO THE INTERNATIONAL WORKSHOP ON POLYMER SCIENCE AND POLYMERIC MATERIALS**

On behalf of the Organizing Committee, let us to welcome you on the workshop of cooperating Institutes from Poland, Hungary and Slovak Republic.

It is our pleasure and privilege to meet you at the International Workshop on Polymer Science and Polymeric Materials, which is held at Centre of Polymer and Carbon Materials, Polish Academy of Sciences in Zabrze. The aim of this workshop is to exchange of experience between the cooperating Institutes and discuss current research on the characterization, modification and application of biocompatible polymers.

We believe that this initiative will help us to develop the closer cooperation among our Institutions and to improve the competitiveness in the attracting international projects.

We very much look forward seeing you this November in Zabrze!

Kind regards,

Organizing Committee

B. Trzebicka, CMPW PAN (Zabrze, Poland)

G. Adamus, CMPW PAN (Zabrze, Poland)

J. Kronek, PI SAS (Bratislava, Slovakia)

T. Feczko, HAS CRNS IMEC (Budapest, Hungary)

J. Rydz, CMPW PAN (Zabrze, Poland),

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M. Kawalec, CMPW PAN (Zabrze, Poland)

## ***Acknowledgement***

This Workshop is supported by Polish-Slovak joint research project for years 2016-2018 “Advanced MD-LC-MS for characterization of biopolymers and their degradation products”, Polish-Hungarian joint research project for years 2017-2019 “Controlled release and degradation studies of biodegradable aliphatic polyester derivatives based nanoparticles loaded with organic drug” and the National Scholarship Programme of the Slovak Republic for the support of mobility of students, PhD students, university teachers, researchers and artists.

## PROGRAMME

**November 10, 2017**

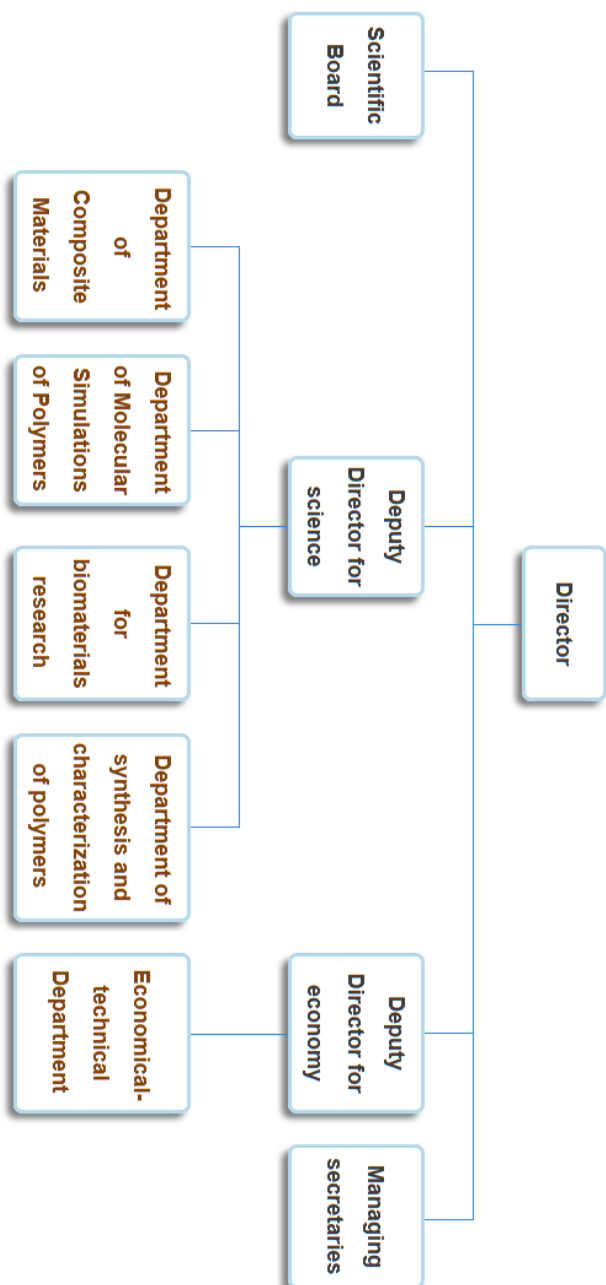
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|---------------|--|
| 10.00 – 10.15 | <b>WELCOME</b><br>B. Trzebicka (Poland)  |
| 10.15 – 11.45 | <b>MORNING SESSION</b><br>G. Adamus (Poland)   |
| 10.15 – 10.45 | Biomedical polymers based on functional 2-oxazolines<br>(J. Kronek, Slovakia)  |
| 10.45 – 11.15 | Complexation of selected biologically active compounds by<br>chosen cyclic oligosaccharides<br>(J. Jaworska, Poland) |
| 11.15 – 11.45 | Applications of thermal analysis in materials science<br>(L. Trif, Hungary)  |
| 11.45 – 13.00 | <b>COFFEE BREAK &amp; POSTER SESSION</b>   |
| 13.00 – 14.15 | <b>AFTERNOON SESSION</b><br>L. Trif (Hungary)  |
| 13.00 – 13.30 | Natural polymers for innovative applications<br>(A. Šišková, Slovakia)   |
| 13.30 – 14.00 | Biodegradable amphiphilic copolymers and hydrogels<br>(M. Kawalec, Poland)   |
| 14.00 – 14.15 | <b>CLOSING REMARKS</b><br>J. Kronek (Slovakia)   |

## **Polymer Institute of Slovak Academy of Sciences** **Bratislava, Slovakia**

Polymer Institute SAS represents an important research and training center for fundamental and applied research in the contemporary topics of polymer chemistry. The Institute activities cover four areas: synthesis and characterization of polymers, composite polymeric materials, polymeric biomaterials and molecular simulation of polymers.

The institute provides the specialized services, which include consultations, infrastructure and innovative solutions for partners from academic institutions, universities and industry both nationally and internationally. Nationally, the institute has a significant position in the area of polymer science and disseminates the information to the public about research activities, obtained results and applications.





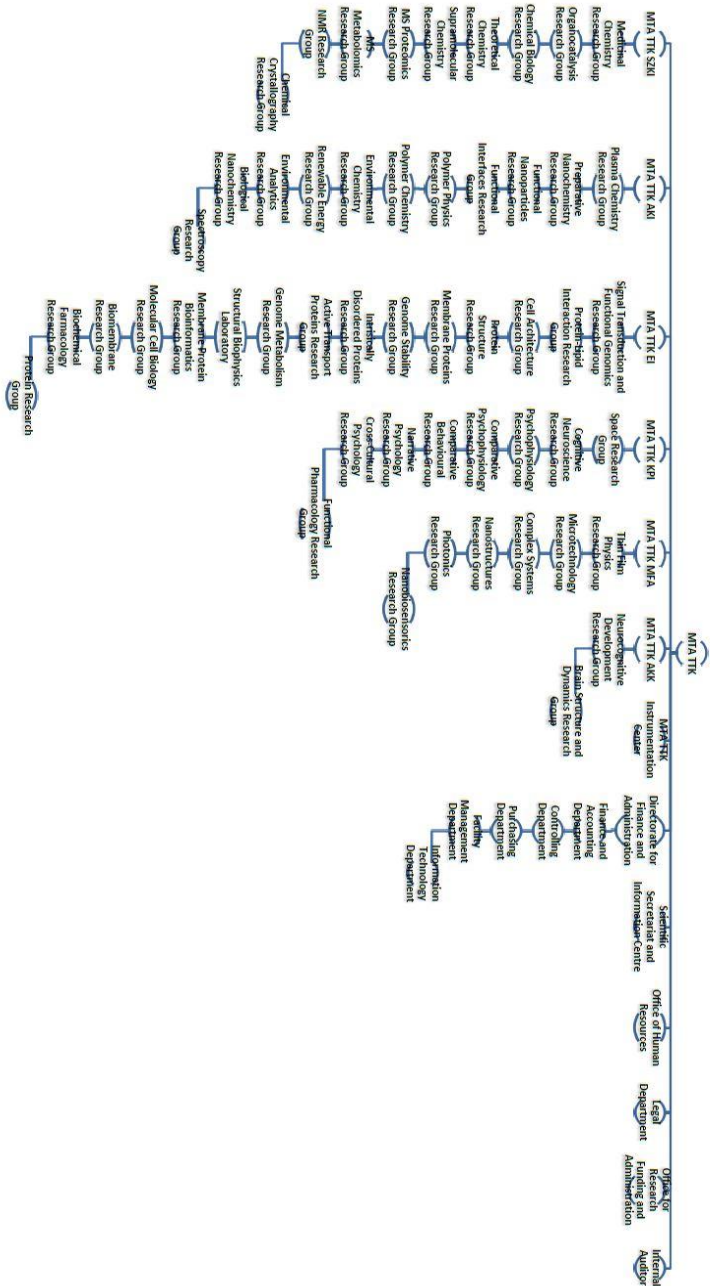


## **Research Centre for Natural Sciences of Hungarian Academy of Sciences Budapest, Hungary**

The Research Centre for Natural Sciences has carried out multidisciplinary research activities in natural sciences, particularly in the fields of enzymology, organic chemistry, molecular pharmacology, cognitive neuroscience and psychology, as well as materials- and environmental chemistry and technical physics and material science.

The main research profile of Institute of Materials and Environmental Chemistry includes functional and structural materials; micro- and nanosized functional particulate systems, surface layers and solid/liquid interfaces in order to reveal correlations among their chemical composition, structure, properties and methods of preparation. Developing new procedures and methods to decrease the environmental impact of technologies, waste treatment and corrosion protection as well as understanding and interpretation of pollution-induced chemical processes in the atmosphere also belong to the main research topics. Extensive study of energy storage and transformation, and the exploitation of renewable energy resources are also aimed.

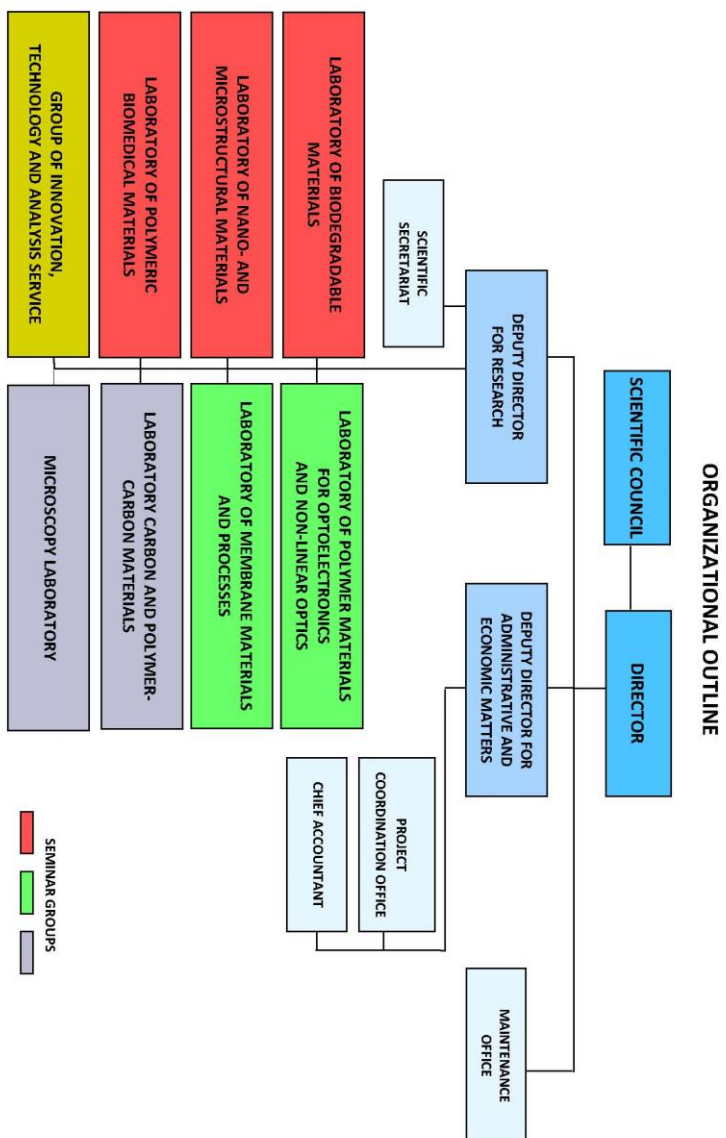




**Centre of Polymer and Carbon Materials**  
**Polish Academy of Sciences**  
**Zabrze, Poland**

The Centre of Polymer and Carbon Materials (CMPW) is an institute of the Polish Academy of Sciences conducting interdisciplinary scientific research regarding polymers, various carbon forms, obtaining and testing the properties of new polymer and carbon materials. The Centre carries out an interdisciplinary character and covers a wide range of topics related with such areas of science as chemistry, physics, biology and medicine. They include studies on the synthesis of new polymer materials with a controlled structure and on their application: in the construction of nano- and microdevices, in selective transportation processes and the controlled release of biologically active substances, in the construction of materials for optoelectronics and molecular electronics, as well as studies on the technology of applying thin layers and the synthesis of monolithic, porous carbon materials as precursors of catalyst carriers for ecological materials and catalysts themselves, and studies on obtaining polymer materials from renewable resources and biodegradable materials.





## **ORAL PRESENTATIONS**

## Biomedical polymers based on functional 2-oxazolines

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Poly(2-alkyl-2-oxazoline)s (POx) belong to a class of biomedical polymers due to their excellent biocompatibility, low (immuno)toxic effects, and stealth behavior.<sup>1,2</sup> Moreover, their preparation via living cationic ring-opening polymerization of 2-oxazolines enables to control over size, topology and functionality of polymers.

Our effort is recently focused on the synthesis of functional POx for drug and gene delivery systems, hydrogel preparation, and conjugates with bioactive molecules. In this contribution, several examples of functional POx will be presented. POx bearing double bond provide thiol-ene “click” reaction suitable for a hydrogel formation or preparation of bioconjugates.<sup>3</sup> Polymers with free 2-oxazoline ring in the side chain also represent promising reactive polymers for biomedical applications.<sup>4</sup>

### **Acknowledgement**

*Author is thankful the Slovak Grant Agency VEGA and Slovak Research and Development Agency for the financial support in the projects No. VEGA 2/0163/15 and No. APVV 15-0485.*

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## COMPLEXATION OF SELECTED BIOLOGICALLY ACTIVE COMPOUNDS BY CHOSEN CYCLIC OLIGOSACCHARIDES

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Katarzyna Jelonek<sup>1</sup>, Arkadiusz Orchel<sup>4</sup>, Piotr Kurcok<sup>1</sup>

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Cyclodextrins (CDs) are cyclic oligomers comprising of glucopyranose units and their molecules have a conical shape with ability to form inclusion complexes. CDs have been widely employed for many purposes in: food, cosmetic and pharmaceutical industries for encapsulation of several substances.<sup>1</sup> Nuclear Magnetic Resonance Spectroscopy (NMR) is a useful technique to study interactions of cyclodextrins with guest compounds- by the observation of the difference in the proton chemical shifts between the free guest and host species and the suggested complex. In this study the complexation of the gentamicin, amoxycilin, doxorubicin by  $\beta$ -CD and  $\gamma$ -CD has been analyzed according to the NMR technique. NMR titration experiments have shown that doxorubicin forms strong complexes with  $\gamma$ -CD, contrary to  $\beta$ -CD.

### Acknowledgement

The work is the result of the research project No. 2015/17/B/ST5/01086 funded by the National Science Centre

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## APPLICATIONS OF THERMAL ANALYSIS IN MATERIALS SCIENCE

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Whenever a sample of material is to be studied, one of the easiest tests to perform is to heat it. In the simplest case, the temperature of the sample may increase without any change of form or chemical reaction. In short, it gets hotter. For many other materials, the behaviour is more complex. When ice is heated, it melts at 0°C and then boils at 100°C. When sugar is heated, it melts, and then forms brown caramel. Heating coal produces inflammable gases, tars and coke. The list is endless, since every material behaves in a characteristic way when heated.<sup>1</sup> The term thermal analysis (TA) is generally used to describe analytical experimental techniques which investigate the behavior of a sample as a function of temperature. The ability of TA to characterize quantitatively and qualitatively a huge variety of materials over a considerable temperature range has been pivotal in its acceptance as an analytical technique.<sup>2</sup> A short overview of the main members of the family of thermal methods, such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) will be presented. Various examples will also be shown from the field of polymers<sup>3</sup>, catalysis, organometallic chemistry and ceramics.

### **Acknowledgement**

The financial support of the exchange agreement between the Hungarian Academy of Sciences and the Polish Academy of Sciences (grant number NKM 103/2017) is greatly acknowledged.

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## NATURAL POLYMERS FOR INNOVATIVE APPLICATIONS

Alena Šišková<sup>1</sup>, Erika Kozma<sup>2</sup>, Francesco Galeotti<sup>2</sup>, Andrej Opálek<sup>3</sup>,  
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The use of natural materials for biochemical applications has increased notably in the last years, due to their biocompatibility combined with exceptional physical, mechanical and chemical properties. Among these materials, silk fibroin from *Bombyx mori* is a natural polymer having outstanding mechanical robustness, high optical transparency and compatibility with living systems. For these reasons, it is widely explored as functional material in surgery, have potential application in fields such as tissue engineering, drug release systems, implantable electronics, microfluidic devices, optics and photonic systems.

In this study we present the preparation of the functional materials that are based on silk carriers produced by electrospinning. The encapsulation of the sodium salt of diclofenac into the silk filaments is studied for the sustained release of the drug. Diclofenac is an anti-inflammatory drug applied to reduce inflammation and as an analgesic. Silk fibers can be modified chemically too, altered through hydroxyl, amino and carboxyl side groups. An efficient and highly specific “click” reaction is widely used for modification in medicinal applications.

### **Acknowledgement**

This work was supported by a Polish-Slovak joint research project “Advanced LC-MS<sup>n</sup> for characterization of bio-polymers and their degradation products”, as well as by SAS-CNR joint research projekt „Nanosilk” (Danko/Galeotti) and by projects VEGA No. 2/0158/17 and APVV No. 15-0528.

## Biodegradable Amphiphilic Copolymers and Hydrogels

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One of the most often investigated polymers for temporary biomedical applications are aliphatic polyesters comprising of lactides and/or glycolide and/or  $\epsilon$ -caprolactone units as well as aliphatic polycarbonates.<sup>1</sup> The polymers own their popularity to the biodegradable and biocompatible character as well as commercial availability of the monomers, which in conjunction with developed polymerization techniques,<sup>2</sup> gives access to materials of wide range of properties. However, improvement of their hydrophilicity is based, in general, on poly(ethylene glycol) blocks incorporation.

Herein, application of functional monomers for biodegradable hydrophilic materials<sup>3</sup> synthesis is discussed. Examples of graft polymer synthesis are also given.

### **Acknowledgement**

A financial support has been provided by Foundation for Polish Science: Homing Plus 2013/7/7 co-financed by the European Union within the Innovative Economy Programme and the National Scholarship Programme of the Slovak Republic for the support of mobility of students, PhD students, university teachers, researchers and artists.

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## **POSTER PRESENTATIONS**

## Partially biodegradable polymer hybrids based on MWNTs

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Vlasta Sasinková<sup>3</sup>, Matej Mičušík<sup>1</sup>, Peter Kasák<sup>4</sup>, Jaroslav Mosnáček<sup>1</sup>

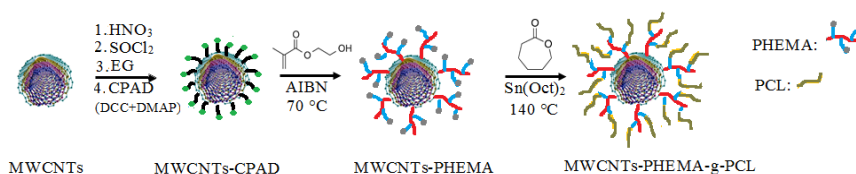
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Controlled living polymerization techniques providing considerable control over both the molecular mass of the surface grafted polymer and polymer grafting densities. Additionally, the combination of radical living and anionic polymerization techniques was successfully applied for preparation of core-shell multilayered hybrid nanoparticles with well-defined structure. Surface initiated reversible addition and fragmentation chain transfer polymerization (RAFT) of HEMA was mediated by both free and MWNTs-immobilized RAFT agent, 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPAD). The pendant hydroxyls of grafted PHEMA were subsequently used for initiation of ring opening polymerization of  $\epsilon$ -caprolactone in bulk under tin (II) 2-ethylhexanoate catalysis. The structure and grafted (co)polymer quantities of MWNTs-PHEMA-g-PCL were characterized by GPC, XPS, TGA, AFM, FTIR and Raman spectroscopy.



### Acknowledgement

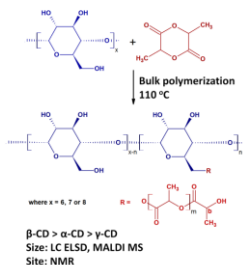
This research was supported by a Polish-Slovak joint research project “Advanced LC-MS” for characterization of bio-polymers and their degradation products” as well as by project SAS-MOST JRP 2014-9 and by project POLYFRIEND no. HUSK 1101/1.2.1/0209 within Hungary-Slovakia Cross-border Co-operation Programme 2007-2013 funded by the ERDF.

# MALDI MASS SPECTROMETRY ASSESMENT OF OLIGOLACTIDE MODIFIED CYCLODEXTRINS

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Cyclodextrins (CDs) are considered ideal candidates in a green chemistry approach for the ring opening (RO) of cyclic esters where they perform a dual role, to activate and to initiate, respectively, the RO reaction<sup>1,2</sup>. The practical importance of such reactions may reside in the pseudo enzymatic activity of CD, but, so far, the actual implication of CD in RO is poorly understood. Nevertheless, uncovering of the intimate structure of the CDs derivatives resulted from such reactions represent a key step in revealing the intimate mechanisms behind the RO of cyclic esters in presence of CDs. The pioneering studies proposed that the RO reaction, in bulk, results in the formation of CDs derivatives having a single chain attached in spite of the multitude of OH groups present on CD molecule. Also, it was claimed that a selective substitution of CDs takes place on the larger rim, at C2. Being given the complexity of the mixtures resulted from such reactions, we considered



useful to have a closer look into the chemical nature of the resulted products using thorough characterization techniques like MALDI and ESI mass spectrometry, liquid chromatography and NMR<sup>3-6</sup>. The analyzed compounds are CDs modified with oligoesters obtained through “green” RO reactions of L-lactide. Our results, here highlighted for the CD-lactide derivatives, support the multiple site substitution on the smaller rim of CD.

**Acknowledgement:** The work is financed from the SASPRO Programme of Slovak Academy of Sciences (Grant Agreement No.: 1628/03/02). Part of the research leading to these results has received funding from the People Programme (Marie Curie Actions) European Union's Seventh Framework Programme under REA grant agreement No. 609427.

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## SYNTHESIS OF NEW THIAZOLO[5,4-D]THIAZOLES FOR SEMICONDUCTING MATERIALS

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The development of organic semiconductors for optoelectronic applications by alternating donor and acceptor units is the most common approach for the synthesis of low band gap materials. Thiazolo[5,4-d]thiazoles (TzTz), characterized by a rigid and coplanar structure, high stability and good electron acceptor properties are valuable starting materials for the design of electron accepting semiconductors. The use of TzTz derivatives for various optoelectronic applications like OLEDs, OFETs, emitters and fluorescent sensors, has been already demonstrated.<sup>1,2</sup>

Following this concept, in this work we describe the synthesis and characterization of thiazolo-thiazole based semiconducting molecules and oligomers. Various aromatic aldehydes and dithiooxamide were used as starting materials in different reaction conditions. Two oligomers were prepared by Suzuki coupling reaction, but the attempt for polymer synthesis failed due to low solubility of starting thiazolo[5,4-d]thiazoles. According to their optical and electrochemical properties, their applications in optoelectronics will be demonstrated.

### **Acknowledgement**

This work was supported by the Slovak Grant Agencies VEGA project No. 2/0161/17 and by bilateral project SAS-CNR (Danko/Galeotti).

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## Heterogeneous materials based on 6FDA-polyimides and MFI zeolite for membrane gas separation applications

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Two types of aromatic polyimides (PI)s based on 6FDA dianhydride were used as polymer matrices, in which 15 wt.% of MFI zeolite particles were dispersed. Polyimides were synthesized by high-temperature polycondensation reaction using two different diamines: 4,4'-(4,4'-isopropylidenediphenyl-1,1'-diylldioxy)dianiline and 4,4'-methylenebis(2,6-dimethylaniline). The chemical structure of these polymers was confirmed by means of  $^1\text{H}$  NMR and ATR FTIR spectroscopy. The polymer films were characterized WAXD, DSC and TGA techniques. The structure of the commercial MFI particles was confirmed by FTIR and XRD methods. The porous character of MFI was investigated using  $\text{N}_2$  adsorption/desorption isotherms. The obtained materials filled with MFI particles were tested by WAXD, DSC, AFM and SEM techniques. Gas transport properties were measured at 30  $^\circ\text{C}$  using gas separation set-up based on constant pressure (variable volume) method. It was found that MFI particles increase gas permeability of both types of membranes in a similar way, independently of the permeability of the neat polyimide matrix. This type of modification resulted in 1.3-1.5 fold increase in  $\text{CO}_2$  permeability with small changes in  $\text{CO}_2/\text{N}_2$  selectivity. This improvement of gas transport properties shows a promising approach for future tailoring of high performance membrane materials.

## PROTONATION EFFECT ON THE OPTICAL PROPERTIES OF PHENYLENE-THIOPHENE POLYAZOMETHINES

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Conjugated polyazomethines are an attractive material for the optoelectronic devices due to their promising optical, optoelectronic, electrical properties together with their simple synthesis and purification. These properties may be further enhanced by protonation of the lone electron pair on the nitrogen atom of the imine bond.<sup>1</sup> This paper presents the changes of UV-Vis absorption, upon protonating the polyazomethines, using trifluoroacetic acid. Three different phenylene-thiophene polymers have been chosen for this experiment, differing in a presence and length of alkoxy side chains. Protonation has been conducted on the polyazomethines both in solid and solution forms. Various mixtures of solvents have been used to investigate the influence of solvent polarity on the protonation process. In investigated systems, the presence of alkoxy group proved to be necessary to successfully protonate the studied compounds. Addition of the acid to a solution of polyazomethine without side groups resulted in degradation of the polymer. Also the length of alkoxy side chains proved to influence the process; longer side groups reduced an access of the acid molecule to the nitrogen atom, slightly hindering the protonation. UV-Vis absorption spectra registered during subsequent addition of trifluoroacetic acid to investigated solutions allowed to observe different stages of the protonation process. Polarity of the solvent also turned out to be an important factor. Only non-polar solvents like chloroform or a mixture of chloroform with n-hexane could support the process. Replacement of the solvent with more polar hindered the process.

### **Acknowledgement**

This work has been supported by the NCN grant (Poland) no UMO-2013/09/B/ST8/01629.

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## INVESTIGATION ON THE SYNTHESIS OF TAILOR-MADE BIOPOLYMER MATERIALS

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Polyhydroxyalkanotes (PHAs) represent an interesting group of biodegradable and biocompatible polymers with a wide range biomedical applications, such as wound treatment, vascular system applications, tissue engineering and drug delivery systems. Despite of a lot of advantages, the PHAs have some drawbacks, such as high crystallinity, brittleness and stiffness which limiting to use of the unmodified PHA in some sophisticated application. To remove these disadvantages, the PHAs are subjected to various chemical modification to obtain from those biopolymers macroinitiators or macromonomers useful in further synthesis protocols.<sup>1</sup>

The presented study are focused on develop a new biomaterials with increased hydrophilicity containing structural units derived from selected PHAs. The first step of synthetic protocol involves controlled degradation of PHAs via a reduction reaction with the aid of lithium borohydride as reducing agent.<sup>2</sup> PHA oligoesterdiols thus synthesized were subjected to further transformation by polyaddition with diglycidyl ester to obtain a new poly(ester-ethers) with desired properties, containing structural fragments of selected PHA, which can not to be obtain on direct biotechnological way.<sup>3</sup>

**Acknowledgement:** This work was supported by the Polish National Science Centre: N<sup>o</sup>. UOM-2013/11/B/ST5/02222.

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## (BIO)DEGRADABLE COMPOSITES FOR SUSTAINABLE FUTURE

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The present challenges related to the design of composites are focused on ensuring their stability during use and at the same time susceptibility to microbial attack during organic recycling.<sup>1</sup> Recent studies indicate a significant effect of the addition of natural fillers on the mechanical properties of the composites, as well as their ability to degrade. Composites composed of biodegradable polymer as matrix and natural fillers as reinforcement have attracted great attention in environmental protection.<sup>2</sup>

The degree of degradation of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) and its composites with cork incubated in abiotic conditions and under industrial (Biodegma system) and laboratory composting conditions was investigated. The addition of cork had influence on the increase of the thermal stability of the obtained composites, what is connected with smaller reduction of molecular mass during processing. This phenomenon had also an influence on the composites degradation process.

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## Synthesis and properties of nucleic acid polyplexes based on star-shaped P(DMAEMA-OEGMA-OH)

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The design of star polymer/nucleic acid polyplexes which represent an smart alternative to viral vectors for cell transfection have made significant progress in the therapies of genetic materials [1].

This work included the preparation of nucleic acid polyplexes based on star polymers with arms made of random copolymer of N,N'-dimethylaminoethyl methacrylate (DMAEMA) and oligo(ethylene glycol) methacrylate with terminal OH moieties (OEGMA-OH). Stars with different OEGMA-OH content and molar masses up to 350 000 g/mol were synthesized using ATRP and "core-first" method. Star-like polymers were studied for delivery of nucleic acids in HT-1080 cells.

The star polymers were complexed with DNA and RNA in particles with the hydrodynamic diameter up to 450 nm dependent on the molar ratio of nitrogen groups of polycation to phosphate groups of nucleic acid. The transfection efficiency was increasing with arm lengths preserving simultaneously the tolerable viability of transfected cells.

### Acknowledgement

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## THERMORESPONSIVE STAR POLYMETHACRYLATES - IN THE SOLUTION AND ON THE SURFACE

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Recently, the thermoresponsive star-shaped polymers based on methacrylates have been widely used due to the development of smart materials. Their compact structure and the multiple functionality is useful for application as carriers for biomolecules in controlled-release systems or as tools in cell sheet engineering. <sup>[1,2]</sup>

Herein we report, synthesis of thermoresponsive star-shaped polymethacrylates with core-shell structure via atom transfer radical polymerization, using the „core-first“ method. Furthermore, their behaviour in the solution and on the solid surface is described. Star-like polymers composed of poly(ethylene glycol methyl ether) methacrylates arms of different length and hyperbranched poly(arylene oxindole) core turned out to be thermosensitive. <sup>[3]</sup> The stars existed as isolated macromolecules in acetone and in water below  $T_{cp}$ . Above  $T_{cp}$ , depending on the concentration, aggregates of stars were obtained. The results of encapsulation of hydrophobic dye in hydrophobic core of isolated stars was successfully.

Thermosensitive stars with arms modified with glycidyl methacrylate groups were covalently attached to solid surfaces using "grafting to" method. Obtained nanolayers were used for adhesion, proliferation and detachment of human fibroblast, controlled merely by the change of temperature.

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## EFFECT OF CHEMICAL STRUCTURE OF THE FUNCTIONALIZED AZO POLY(ESTER IMIDE)S ON THE SELECTED PROPERTIES

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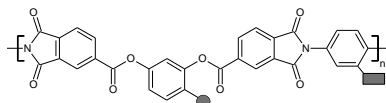
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Despite the research conducted over the past two decades, the azopolyimides are becoming increasingly popular, this is due to their interesting properties (high mechanical strength, excellent thermal stability and high chemical resistance). They are investigated for many applications e.g. as materials for optical data storage and as liquid crystals photoalignment layers<sup>1</sup>. Their potential applications result from reversible trans-cis photoisomerisation reaction, which leads to photoinduced optical anisotropy<sup>2</sup>.



The work presents a series of amorphous azopolymers differing in chemical structure - chromophore position within the backbone (either between the ester or the imide groups) and the chromophore concentration (one or two per a structural unit), Fig 1. The purpose of investigations was description relationships between the azobenzene location and its concentration within the backbone and selected properties of azopolyimides,

Poly (ester imide) code		
PI-1	H	
PI-2		H
PI-3		

Fig 1. Chemical structures and codes of the studied poly(ester imide)s

such as optical (UV-Vis), thermal (TGA, DSC) and the photoinduced birefringence and their stability in the dark<sup>3</sup>.

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## Study of the chain transfer reaction in anionic ROP of $\beta$ -butyrolactone initiated with carboxylic acid salt

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Poly([R]-3-hydroxybutyrate) is the most common member of polyhydroxyalkanoates (PHAs) *i.e.* a class of biodegradable aliphatic polyesters synthesized by bacteria.<sup>1</sup> Biomimetic poly(3-hydroxybutyrate) can be prepared also *via* anionic ring-opening polymerization (ROP) of  $\beta$ -butyrolactone (BL).<sup>2</sup> The process is controlled though chain transfer reaction occurs. There are two types of the chain transfer reaction mechanisms claimed in the scientific literature: either to monomer or to polymer.<sup>3</sup> Simple distinguishing is impossible because of the same products. Herein, model compound: cinnamate ester of ethyl 3-hydroxybutyrate; was prepared and BL ROP initiated with tetrabutylammonium acetate was carried out in presence of the model compound. In result, it is demonstrated that crotonate end groups are formed at the very beginning of the polymerization process as a consequence of the chain transfer reaction to the monomer.

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## NEW METHOD OF STABILIZATION OF MESOGLOBULES AND ITS POSSIBLE UTILIZATION

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Mesoglobules - spherical particles formed by thermoresponsive polymers - are stable above the transition temperature ( $T_{CP}$ ) while below this temperature they disintegrate. Previously mesoglobules were stabilized by nucleated radical polymerization in which they were coated by polymer shell.<sup>1</sup> It was shown that two types of thermoresponsive chain mixed in aqueous solutions could form mixed particles.<sup>1</sup>

The aim of this work was to stabilize mixed mesoglobules by crosslinking two types of polymer chains. The crosslinking was performed by Huisgen 1, 3-dipolar cycloaddition of azides and alkynes. The mixed mesoglobules were made of thermoresponsive polymers of oligoethylene methacrylates and 2-aminoethyl methacrylate with functional azide groups P(D-co-O-co-A\_Az) or 2-propyn-1-yl carbamate groups P(D-co-O-co-A\_Pr). The obtained crosslinked particles were stable below phase transition temperature.

This approach was used to prepare nanocarriers of doxorubicin. Doxorubicin was connected with P(D-co-O-co-A\_Az) by triazole ring in Huisgen reaction. Then the nanoparticles were formulated by aggregation of the bioconjugate and respective partner.

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## SYNTHESIS OF PROPARGYL-FUNCTIONALIZED BIODEGRADABLE COPOLYMERS FOR CLICK-CHEMISTRY REACTIONS

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A six-membered carbonate functionalized with propargyl group (5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one) was synthesized<sup>1</sup> and copolymerized with L-lactide, trimethylene carbonate and  $\epsilon$ -caprolactone using metal-free ring-opening polymerization technique. The study comprises application of various catalytic systems: TBD, DBU and (-)-sparteine/N-3,5-bis(trifluoromethyl)phenyl-N'-cyclohexylamine thiourea<sup>2</sup>. Composition and microstructure of the materials was determined based on NMR measurements.

The presented results will be applied in further work leading to cyclodextrin-functionalized biodegradable polymers.

### Acknowledgement

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## Modification of the surface chemistry of polyester devices

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Polymer devices have become an essential part of our life. Among them, special attention is given to the devices made from biodegradable biomaterials, since they are widely used in medical applications, and therefore are expected to improve or even save human lives. Polylactide, polyglycolide, polycaprolactone, and polyhydroxyalkanoates have become one of the most important polymeric materials used in such applications, especially in tissue engineering and drug delivery systems.<sup>1</sup>

Biomaterials, as defined,<sup>2</sup> are supposed to interact with biological systems, including cells and tissues. Since interactions of cells with biomaterials are greatly influenced by the surface chemistry and topography of the latter,<sup>3</sup> there is a need to modify the surface properties of polymeric materials. For example, scaffold devices made directly from polyhydroxyalkanoates are not appropriate to be placed at the site of defect and that is primarily due to the fact that they are hydrophobic. Moderately hydrophilic surfaces offer better cell attachment and therefore proliferation as compared to hydrophobic ones.<sup>3</sup> In this communication, a method which allows modifying surface chemistry, and hence hydrophilicity of devices made of aliphatic polyesters will be presented.<sup>4</sup>

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## **MECHANICAL PROPERTIES AND BIODEGRADABILITY OF THE POLYMER COMPOSITES WITH NATURAL FILLER**

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In this study, the possibilities to use bran as a natural filler in the composites of biodegradable polymers to form a disposable flower pots and examining their influence on properties of the composite was investigated. Range of the research included the initial survey of samples obtained from the Center of Polymer Chemistry in Zabrze and determine the mechanical properties and influence of water on the composites.

Several types of samples were divided into three groups: gelatin composites, composites with Solublon® and composites containing ENMAT or PLA. The first step in the test was to describe samples by macroscopic examination by the human eye and with a light microscope. Then the samples were subjected to tests of mechanical properties such as static tensile test and hardness test. At the end in order to study the effects of water on composites, wettability test and biodegradability tests were conducted.

The results prove that wheat bran is an alternative to natural fillers. Research shows that all the properties of both the mechanical and the influence of water strongly depend on the content of individual components.

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## Paclitaxel release from bioresorbable co- and terpolymers

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Aliphatic polyesters and polyester carbonates are extensively used in medicine and pharmacy.<sup>1</sup> A huge advantage of such bioresorbable devices is their multifunctionality while they offer accurate adjustment to the anatomical, physiological and, what is also important, the surgical requirements. Apart from tissue scaffolding they may serve as delivery systems of wide range of active substances as antibiotics, steroids or anticancer drugs and be implanted during minimally invasive surgery.<sup>2-3</sup>

The aim of this work was to study paclitaxel (PTX) release from double layer bioresorbable co- and terpolymers synthesized from lactide, glycolide, trimethylene carbonate and  $\epsilon$ -caprolactone. Double layer matrices of various drug percentage content in each layer were obtained and hydrolytically degraded. Paclitaxel released into media was evaluated by high performance liquid chromatography.

Differences between co- and terpolymers in release rates and profiles were observed. This finding may be used to tailor PTX release from bioresorbable delivery systems.

### **Acknowledgement**

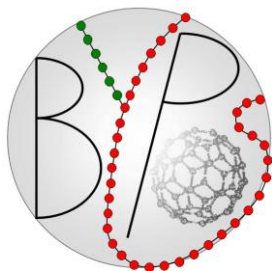
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## 8<sup>th</sup> Young Polymer Scientists workshop

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## NOTES

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