11th ECNP International Conference on Nanostructured Polymers and Nanocomposites

August 28-31, 2023
Lodz, Poland

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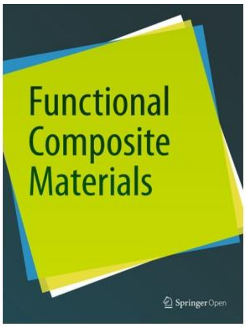
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14:15 – 14:55	**PL1: Krzysztof Matyjaszewski,** CMU, Pittsburgh, USA and DMP, TUL, Lodz, Poland *Nanostructured polymers and nanocomposites by ATRP*
14:55 – 15:25	**KL1: Rebeca Hernandez,** *Institute of Polymer Science and Technology,Spanish.* CSIC, Madrid, Spain *Tuning the structural and rheological properties of polymer hydrogels for 3D extrusion bioprinting and injectable biomaterials*
15:25 – 15:50	IL1: **Jens Gaitzsch**, IPF, Dresden, Germany *Functional polyesters from radical ring-opening polymerization by structural understanding and additional monomers*
15:50 – 16:10	OR1: **Piotr Ślęczkowski,** ICRI-BioM, TUL, Lodz, Poland *Triphenylene-tricarboxyamide based supramolecular polymers: from solution to surface studies*
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Session 2: Advanced processing of polymer nanocomposites ***Dedicated to the memory of Professor Jean-Pierre Pascault*** **Chairperson: Cristina Elizetxea Ezeiza**	
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10:05 – 10:30	IL4: **Adam Proń**, WUT, Warsaw, Poland *New electroactive inorganic/organic hybrids: synthesis, spectroscopic properties and application in visible light photocatalysis*
10:30 – 10:50	OR4: **Guillermo Martinez-Denegri,** ICRI-BioM, TUL, Lodz, Poland *Understanding the role of molecular interactions in the emission of two ESIPT isomers for thin film applications*
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Session 4: Polymers for biological and biomedical applications **Chairperson: Carmen Mijangos**	
11:20 – 11:50	**KL3: Brigitte Voit**, IPF, Dresden, Germany *Multiresponsive hydrogels as smart materials for actuator and sensor functions in microfluidic application*
11:50 – 12:15	IL5: **Ileana Rău**, University POLITEHNICA of Bucharest, Bucharest, Romania *DNA – Based Materials – Intriguing Materials for Nonlinear and Lasing Applications*
12:15 – 12:35	OR5: **Joanna Pietrasik,** IPDT**,** TUL, Lodz, Poland *Oligo(ethylene glycol) methyl ether methacrylate based hydrogel with intrinsic antimicrobial activity against Pseudomonas aeruginosa as a model of a major wound infecting human pathogen*
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15:00 – 15:25	IL6: **Agata Blacha-Grzechnik**, Silesian University of Technology, Gliwice, Poland *Electrochemically deposited organic layers as light-activated antimicrobial coatings*
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17:30 – 17:45	OR10: **Szymon Stolarek**, Xenocs SAS, Grenoble, France *SAXS/WAXS mapping of nanostructured polymers: from image to nanostructure*
17:45 – 18:00	OR11: **Peter Schön,** Bruker, Germany *Latest developments in atomic force microscopy for polymer research*
18:00 – 18:20	OR12: **Piotr Polanowski**, DMP, TUL, Lodz, Poland *The DLL (Dynamic Lattice Liquid) model. How it works?*
18:20 – 18:45	IL7: **Andrzej Sikorski**, University of Warsaw, Warsaw, Poland *Studies of the polymerization process of branched polymers based on Monte Carlo simulations*
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10:15 – 10:35	OR14: **Tomasz Marszałek,** MPI-P, Mainz, Germany and DMP, TUL, Lodz, Poland *Optimized charge transport in molecular semiconductors by control of fluid dynamics and crystallization in meniscus-guided coating*
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12:15 – 12:40	IL11: **Debora Puglia,** University of Perugia, Terni, Italy *Multifunctional bionanocomposites based on lignin and its hybrids: use in packaging, biomedical and agriculture sectors*
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09:55 – 10:15	OR16: **Przemysław Data,** DMP, TUL, Lodz, Poland *Electrochemically tailored conjugated polymers as materials for electrochromic windows and OLED emitters*
10:15 – 10:35	OR17: **Jiyong Kim**, Fraunhofer Institute for Applied Polymer Research, Potsdam, Germany *InP-based Quantum Dots in light emitting diodes: connectivity of device performance and surface chemistry*
10:35 – 11:00	COFFEE BREAK
Session 10: Printed and wearable electronics **Chairperson: Beata Łuszczyńska**	
11:00 – 11:25	IL13: **Argiris Laskarakis**, Aristotle University of Thessaloniki and Center of Organic & Printed Electronics-Hellas, Thessaloniki, Greece *Automated roll-to-roll manufacturing of printed Organic Photovoltaics through In-line Metrology*
11:25 – 11:50	IL14: **Gert-Jan Wetzelaer**, MPI-P, Mainz, Germany *Efficient single-layer blue organic light-emitting diodes*
11:50 – 12:10	OR18:**Petra Pötschke,** IPF, Dresden, Germany *PMMA as blend partner in PA6/carbon nanotube composite: Effect on morphology, rheology, and thermoelectric properties*
12:10 – 12:30	OR19: **Jacek Ulański**, DMP, TUL, Lodz, Poland *Controlling the morphology of thin layers of crystalline organic semiconductors*
12:30 – 12:50	***Closing of the conference***

PLENARY LECTURES

Nanostructured Polymers and Nanocomposites by ATRP

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Various nanostructured functional materials were recently designed and prepared by controlled/living radical polymerization. Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands are among the most efficient controlled radical polymerization systems. By applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers was controlled by various external stimuli, including electrical current, light, mechanical forces and ultrasound, also in the presence of ambient air in open flask systems. ATRP was employed for synthesis of polymers with precisely controlled molecular architecture with designed shape, composition and functionality. Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials, bioconjugates as well as nanocomposites were prepared with high precision. Some examples of applications of these materials in areas related to energy, environment and biomedicine will be presented.

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Carbon Nanostructures by Design

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Benzene is a universal module of polymer chemistry. It occurs in linear polyphenylene chains, graphene sheets and dendrimer spheres. In each case, precision polymer synthesis, sometimes applying sophisticated protocols of organic chemistry, is an essential tool.

Linear poly-para-phenylenes are the prototypes of conjugated polymers, but often exist as ill-defined structures. A precursor route is introduced which uses kinked benzene derivatives for solubilization. This technique affords defect-free and high molecular-weight polymer chains in a regular lamella-type packing.

Graphenes and their quasi-1D subunits, the graphene nanoribbons (GNRs), can be made using another precursor protocol. This starts from highly branched polyphenylenes which are then subjected to an electron-transfer induced dehydrogenation („graphitization"). GNRs can be 600 nm long and several nm wide, but still be solution processable.

Finally, polyphenylene dendrimers (PPDs) are obtained as unique shape-persistent 3D-particles with molecular weights as high as 1.9 MDa by way of repetitive Diels-Alder cycloadditions utilizing AB_2 and AB_4 branching reagents.

Synthetic breakthroughs open the door to unprecedented functions. GNRs are the long sought-after link between conjugated polymers and graphenes. Due to their tunable electronic band gaps, they are effective semiconductors, but can also give rise to topological insulators and are essential for new computing techniques. PPDs, in turn, when being decorated with patched surfaces from alternating polar and unpolar groups, are efficient vehicles for gene transfection.

[1] Science 2019, **366**, 1107;
[2] Nature Nanotechnology 2020, **15**, 22;
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[4] Nature Rev. Chem. 2017, **2**, 01000;
[5] Nature Synthesis 2022 , **1**, 289;
[6] Progr. Polym. Science 2022, 123, art. No 101489;
[7] Nature Chemistry 2021, **13**, 581;
[8] Progr. Polym. Sci. 2022, **123**, art. no 101489;
[9] J. Amer. Chem. Soc. 2022, **144**, 11499;
[10] ChemistryEur. J., 2023, e202203735;
[11] Nature Materials, 2023, **22**, 180.

KEYNOTE LECTURES

KL1

Tuning the structural and rheological properties of polymer hydrogels for 3D extrusion bioprinting and injectable biomaterials

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In the Nanostructured Polymers and gels group at the institute of Polymer Science and Technology (CSIC), we are dedicated to improve and engineer polymer hydrogels through mastering of the chemistry and rheological properties to introduce novel advanced functional materials such as 3D printing biomaterial inks and injectable hydrogels [1,2].

In this presentation, I will present a selection of recent research studies from my lab focused on the use of dynamic covalent bonds as a means to engineer injectable hydrogels from hyaluronic acid, the employment of complex coacervation between polysaccharides and proteins to produce a set of biomaterial inks to be used as 3D scaffolds in cell culture studies and the development of sacrificial inks based on star copolymers of polyethylenoxide and polycaprolactone emphasizing on the effect of architecture on gel formation and printability (Figure 1).

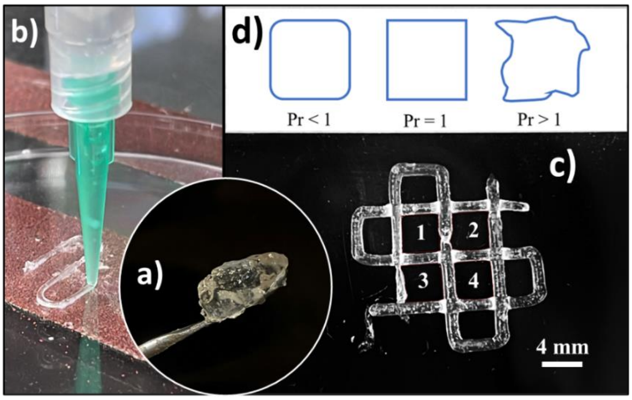

Figure 1: a) Physical appearance of an hidrogel of a 4-arm star copolymer of polycaprolactone and polyethylenoxide, $(\mathrm{PEO}_{1.2}\text{-}b\text{-}\mathrm{PCL}_{1})_{4}$, b) 3D extrusión printing (ϕ:0.8 mm), c) Printed grid for determination of printability index (Pr), d) Variation of Pr[3]

This research was funded by the project PID2020-113045GB-C22 funded by MCIN/ AEI /10.13039/501100011033

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[3] Bom, S., Ribeiro, R., Ribeiro, H. M., Santos, C. & Marto, J. *International Journal of Pharmaceutics* **(2022)**, 615, 121506.

Combining Sol-Gel Chemistry, Metal-Oxo Clusters, and Ionic Liquids for Nanostructured Polymer Networks

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It is now recognized that nanoscale structuring of polymers, particularly high-value polymers such as polymer networks, is a versatile way of introducing several functionalities that may be antagonistic. This approach involves the introduction of nanobuilding blocks that individually provide specific functions: optical, mechanical (including surface), fire resistance, antibacterial, etc., which can be combined to design multifunctional materials.

The aim of this lecture is to review the different approaches developed within our research team to provide such nanostructures, *i.e.* to design inorganic - hybrid organic-inorganic nanomaterials. The specificity of the polymer systems described is that nanostructuration is applied to polymers derived from reactive systems (polyaddition, free radical polymerization). The nanostructures can therefore *i/* be pre-formed and introduced into the reactive system or *ii/* issued from self-assembly mechanisms and/or (nano)phase separation induced by polymerization reaction. The following routes can be described

- Assembling of ionic liquids as ionic nanostructures within the polymer network [1]
- Generation of inorganic-rich nanostructures by *in-situ* sol-gel chemistry of metal alkoxides [2][3]
- Introduction of metal-oxo nanoclusters as individual (non-reactive or reactive including ionic liquid-functionalized) nano-objects or via organic-inorganic block copolymers synthesized by controlled radical polymerization [4-7].
- Introduction of dynamic bonds (Diels-Alder) on nanoparticles such as boron nitride

along with the (nanoscale)morphologies and the properties of the resulting nanomaterials [8].

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Multiresponsive hydrogels as smart materials for actuator and sensor functions in microfluidic application

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Responsive polymeric materials are becoming a highly studied field especially with regard to their use in technical applications, e.g. as sensors and actuators in microsystems and microfluidic applications, since they are able as volume gels to carry out mechanical work reacting on an e.g. chemical stimulus. In addition, compartimentalization becomes an issue for being able to localize specific actions and reactions e.g. by patterning specific hydrogel compartments. We will report on the preparation and integration of responsive and biocompatible hydrogel dots and hydrogel dot arrays of high flow and shear stability in microfluidic channel and chamber reactors. For that, multiresponsive hydrogels are developed making use of interpenetrating network approach and the concept of graft copolymer networks for retaining responsivity for up to four different stimuli in one hydrogel.[1] The hydrogels have been adapted for integration into microfluidic devices as volume-changing gels, adjusting degree of swelling as well as mechanical stability and allowing their use as effective sensors and actuators as needed for a chemical valve function. First examples of their use as chemical transistors and the development of logical modules for achieving basic logic gate functions through a microfluidic setup.[2] Further optimization has been achieved by combining in double-crosslinked systems permanent and dynamic and reversible crosslinking points introducing redox functions and host-guest interactions.[3] The dynamic responsive behavior could be translated into micrometer hydrogel dots in microsystems combining actuator function with specific bioresponse. First results are presented to use reversible redox bonding in hydrogels for triggered peptides capturing and release,[4] and to adapt hydrogel dots as enzyme carriers in multi-chamber microreactors for complex cascade enzymatic reactions.[5]

Acknowledgements: DFG GRK 1865; Prof. A. Richter and coworkers, Prof. K. Castiglione

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ε-caprolactam "*in situ*" polymerization process for continuous fibre polyamide 6 composite parts-CAPROCAST Technology

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Since 2004, TECNALIA is involved in the development of a new process for composite continuous fibre composites manufacturing. The technology behind the proposed solution (CAPROCAST technology) is the "in situ" polymerization of ε-caprolactam were the caprolactam (monomer of Polyamide 6) is cast or injected at very low pressure in a mold, where continuous fiber preform is placed, to obtain a final part in a one-shot process. This technology provides the capability to produce engineering plastic parts using raw materials (monomers) instead of polyamide pellets. This change implies advantages as cost reduction, elimination of part size limitation and manufacturing energy reduction. On the other hand, the possibility of adding additives like fibers or nanofillers might improve the final product properties. The very low viscosity of the melted monomer allows an easy infiltration/infusion of fabrics and textile preforms, increase the structural behavior of the final part.

Focused in the automotive structural parts as main target to reach, during this time, Tecnalia has been involved in the selection and validation of the most suitable commercial available catalysts systems; selection and study of compatible fibres (aramid, glass and carbon) as reinforcements; design and manufacturing of a laboratory scale casting machine; optimization of process parameters which assures the best composite mechanical performance in the shorter time; realization of a testing campaign (physical, thermal and mechanical) on developed thermoplastic composites and, finally, manufacturing of a laboratory scale prototype as demonstrator of technology potential.

The main results achieved on technology development can be summarized as: i) the control and optimization of matrix polymerization reaction parameters with the aim of obtaining the best mechanical properties of the final parts [1]; ii) materials selection in terms of compatibility. iii) preform manufacturing; iv) manufacturing equipment concept and design [2, 3]; v) mould concept, design, and manufacturing [4]; vi) parts manufacturing; vii) parts testing and validation.

[1] EP 2336665 B1 & US 9,290622 B2. Process and device for polymerizing lactams in molds
[2] EP 2743061 B1. Device for polymerizing lactams in molds (I)
[3] EP 3078465 B1. Device for polymerizing lactams in molds (II)
[4] EP19382954.6A1. Method and system for producing hybrid composite parts

Double polymer brushes studied by molecular simulations

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Polymer brushes have been studied because their unique and fascinating properties for many years. In this presentation we give an overview of physical models for polymer brushes and double polymer brushes. We present both theory and relevant molecular simulations. First, we will focus on the entropy of the brushes in different models. Then we present out selected results concerning structure and dynamics of opposing double brushes coming from molecular simulation [1,2]. Opposing polymer brush systems were synthesized and investigated by molecular modeling. Chains were restricted to a face-centered cubic lattice with the excluded volume interactions only. The system was confined between two parallel impenetrable walls, with the same number of chains grafted to each surface. The dynamic properties of such systems were studied by Monte Carlo simulations based on the dynamic lattice liquid model and using a highly efficient parallel machine ARUZ, which enabled the study of large systems and long timescales. We show a variety of intriguing insights. For example, we predicted and confirmed that in a polydisperse sample, the longer chains have unique configurations consisting of a stretched stem and a coiled crown.

Acknowledgements, Funding from Polish National Science Center - UMO-2017/25/B/ST5/01970

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Polymerization and structure of opposing polymer brushes studied by computer simulations
(2021) Polymers, 13 (24)

Hydration and molecular dynamics in thermo-responsive POEGMAs-based hydrogels

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Stimuli responsive polymers gain a common attention as materials useful for many applications including micro-electro-mechanical devices, artificial tissues, drug carriers, sensors, and many others [1]. Poly(oligo(ethylene glycol) methacrylates) POEGMAs as homologies of poly(ethylene glycol) are especially attractive for medical purposes as biocompatible thermosensitive polymers with a fully reversible answer to stimuli (temperature) manifested by the coil-globule transition (in solutions of linear polymers) or the volume phase transition VPT (in gels) [2]. It was recently shown that VPT in different POEGMA-based systems depends only slightly on the crosslinking degree, while regularity of the network and network decoration by side chains can significantly influence the dynamics of VPT [3].

In this communication, problems related to POEGMA chain hydration will be discussed in detail [4,5]. Polymer-water interactions and various water states in POEGMA hydrogels obtained by radiation-induced polymerisation and cross-linking will be discussed. Vibrational spectroscopic studies are supported by DFT calculations.

The second part of the presentation will be devoted to the molecular dynamics in POEGMAs gels with various oligoether side group lengths. Molecular relaxations of both water molecules and polymer segments will be presented [6].

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Polymeric and composite multifunctional materials in advanced industrial applications

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Electronic Memory Phenomena in Polymers

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Although not desirable in most traditional electronic applications, the hysteresis in current-voltage characteristics often observed in many polymers can be exploited to store information in resistance memory devices. In the case of bistable resistive switching, polymers can be used for resistive random access memory (ReRAM), which works by changing the resistance of a thin layer of polymer, and could be used as memory devices in low-cost printed electronics. Such a two-terminal electronic element that exhibits nonlinear volt-ampere characteristics and a hysteresis during cycling is called a memristor. Its resistance depends on the charge passed through it previously. Due to its structural and functional analogy, the memristor can mimic biological neuronal synapses. The possibility of acquiring multimodal resistive states depending on electrical external stimuli, forms an analogy with the response of synapses and can be used in artificial neural networks and neuromorphic computing.

Memristive elements with the active layer made of polymers containing carbazole as a charge transporting group, either embedded in the polymer chain or attached as a side group, have been reported as promising materials for resistive RRAMs [1]. In these polymers, the resistive switching is assigned usually to voltage induced morphological changes that influence the charge transfer probability between neighboring carbazole molecules. Depending on the operating mode of the memory element, the polymer can operate as a binary memory element or as a memristor. Along with the voltage-induced conformational changes, also other phenomena like redox reactions and trapping/detrapping of charge carriers in the localized levels can play a role.

Memristors with neurosynaptic functionality take a continuity of resistance values with synaptic weights modulated by the number and frequency of homogeneous spikes. In order to mimic neural synapse, memristors must exhibit analog properties including non-abrupt switching transitions, continuously variable resistance states, and predictable response. We present such functionality on thin films of poly(methacrylamide) derivative with charge transporting group separated from the polymer backbone by an alkyl chain and show that electrical characteristics can change from bistable to analog behavior, depending on the layer thickness, electrode material and applied voltage range.

The support of the Technology Agency of the Czech Republic, DP-TN02000067is acknowledged

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INVITED LECTURES

Functional polyesters from radical ring-opening polymerization by structural understanding and additional monomers

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Polyesters as biodegradable polymers can play a key role in solving current environmental challenges. Radical ring-opening polymerisation (RROP) of cyclic ketene acetals (CKAs) presents a synthetic strategy to synthesise functional polyesters with a broad scope of accessible properties like semi-crystallinity, hydrophilicity and pH sensitivity. [1, 2]. Understanding, controlling and overcoming the side reactions and including responsive units are hence key to ready RROP-based polyesters for the future.

One of the side reactions of RROP is the characteristic branching reaction. In polymerising the 2-methylene-1,3-dioxepane (MDO) towards poly-MDO, increasing the branching density systematically decreased the melting temperature, melting heat and also systematically altered the viscosimetric properties of the solution. [3] One way to control the branching density is the monomer conversion during synthesis. For the more hydrophilic 2-methylene-1,3,6-trioxacane (MTC), the branching density of poly-MTC proofed to raise independent of polymerisation conditions.[4] It was also the ideal candidate to be copolymerised with amine-bearing CKAs (MACs) to produce a broad range of pH responsive polyesters.

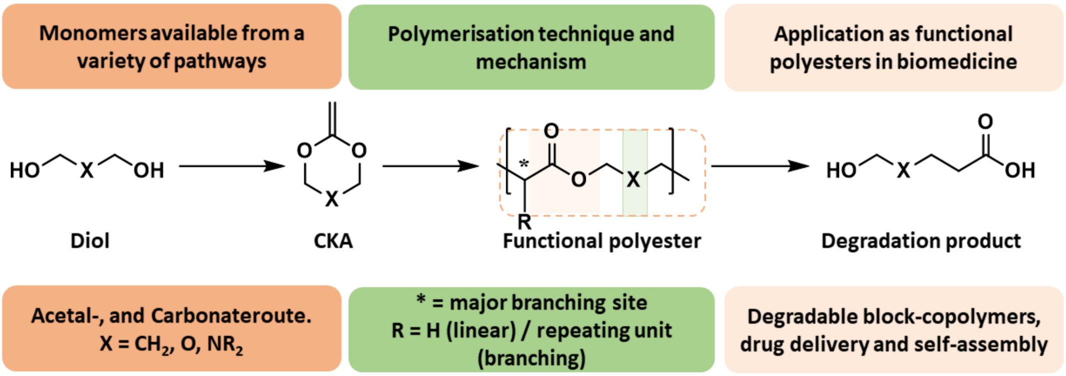

Figure 1: Cyclic ketene acetals (CKAs), originating from diols, polymerize into polyesters through radical ring-opening polymerization. The polyesters then have distinct structural properties like branching units, which affect the macroscopic properties of the materials.

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Nanomechanisms of plastic deformations of polymers, the role of amorphous phase and entanglements of macromolecules.

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Most of commodity polymers are crystalline with lamellar crystals arranged in stacks with alternating amorphous layers, both entities having thickness in a nm range. It is in the interlamellar regions that the initial stage of deformation takes place because of their low modulus [1]. In tension it appeared that one of the main nanomechanisms of plastic deformation is cavitation. Cavitational nanopores are formed within amorphous layers contributing to as much as 20-100% of the material volume. The formation of nanopores is triggered from free volume pores while the rules for cavitation to occur was evaluated by us in the past [2,3]. Cavitation causes the redistribution of stress which results in irregular lamellae shear, fracture and all other phenomena involved in micronecking. Crystallinity degree is a decisive parameter in tensile yielding rather than the crystal resistance.

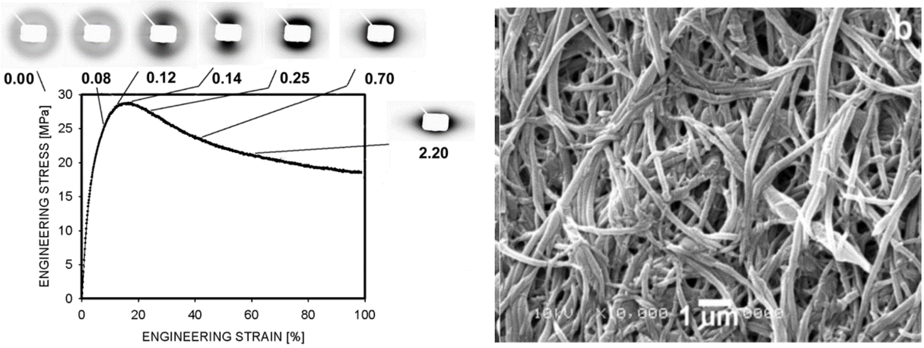

Figure 1: a.) Cavitation detected in small angle X-ray scattering recorded *in situ* at Hamburg synchrotron [2]. b.) nanofibrils obtained from disentangled polypropylene.

Three important implications follow from the above reasoning: (1) no cavitation is observed in polymers with low yield strength, while for polymers with high yield strength cavitation is a rule, (2) applying positive hydrostatic pressure suppresses cavitation, (3) polymers with less entangled macromolecules cavitate very easily [4].The plastic flow can be so easy that disentangled polymer embedded in another viscous media can be deformed into nanofibrils by melt shearing as presented in Figure 1b.

National Science Centre, Poland, is acknowledged for the grant 2021/41/B/ST8/04036.

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Two-dimensional heterostructures of graphene and transition metal oxides for applications in optoelectronics

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Since the breakthrough discovery of graphene, two-dimensional (2D) materials have attracted a lot of attention due to their extraordinary properties in comparison with bulk counterparts. In particular, due to its high electrical conductivity, transparency in the visible range of electromagnetic radiation and flexibility, graphene can be considered as an electrode in the construction of an organic light-emitting diode (OLED). However, pristine, undoped graphene is not suitable for use as an electrode because the work function of graphene is not matched to the energy levels of the organic layers used for OLED fabrication.

Here we show that work function of graphene can be modified with transition metal oxides such as: MoO_3, Re_2O_7 and heterostructures obtained meets the basic requirements for use as a transparent anode in OLED application [1-3]. Additionally, we reveal that crystallinity of 2D materials is a key factor for efficient work function modification.

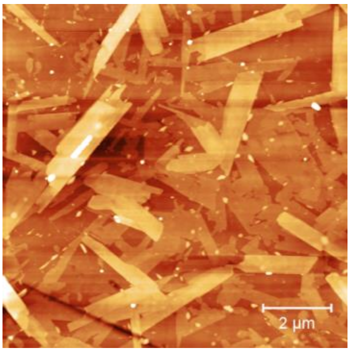

Figure 1: Atomic force microscopy image of 2D MoO_3 islands grown on graphene/quartz

This work was financially supported by the National Science Centre (Poland) under grants 2016/21/B/ST5/00984 and 2020/37/B/ST5/03929

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New electroactive inorganic/organic hybrids: synthesis, spectroscopic properties and application in visible light photocatalysis

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It is demonstrated that nonstoichiometric quaternary Ag-In-Zn-S nanocrystals prepared from $InCl_2$ exhibit composition-dependent selectivity in industrially important processes of aromatic aldehydes and furfural reductions, never reported for this type of nanomaterials. Two sets of nanocrystals were prepared exhibiting red (731 nm) and green (528 nm) photoluminescence, abbreviated as **R** and **G** respectively. These hydrophobic **R** and **G** nanocrystals could be easily transformed into hydrophilic ones through the exchange of their primary ligands for 11-mercaptoundecanoic acid (MUA) ligands, yielding **R-MUA** and **G-MUA** nanoparticles. All studied nanocrystals (hydrophobic and hydrophilic) exhibited long photoluminescence lifetimes implying their potentially promising photocatalytic properties. Photocatalytic reduction of aryl aldehydes, among others furfural, to industrially important alcohols was selected as a test reaction. The reductions were carried out at room temperature either in a nonpolar solvent (C_6D_6) or in water (D_2O) using green LED as a source of radiation. *p*-Toluenethiol and isopropanol were tested as reducing agents and cesium acetate (AcOCs), triethylamine (Et_3N) and potassium *tert*-butoxide (*tert*-BuOK) as bases. In the reaction of furfural reduction hydrophobic **R** nanocatalysts emitting red light (E_g = 2.0 eV) selectively yielded furfuryl alcohol, independently of the applied reducer/base couple. Green light emitting **G** nanocatalysts (E_g = 3.2 eV) in the same test reaction selectively yielded deoxyfuroin as a product of pinacol coupling. Photocatalytic reduction of furfural in aqueous (D_2O) media with *p*-toluenethiol reducer resulted in selective formation of furfuryl alcohol with conversion degrees increasing with increasing strength of the applied base. In the absence of base hydrofuroin was selectively obtained.

DNA – Based Materials – Intriguing Materials for Nonlinear and Lasing Applications

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The laws of the circular economy as well as sustainable development encourage scientists to conduct their research in such a way as to obtain new, eco- friendly materials. In this respect, DNA-based materials continue to be interesting and intriguing materials due to the fact that the deoxyribonucleic acid (DNA) is a "green" material with a fast degradation time in unprotected environments that can be produced from waste of the food industry. Therefore, materials based on the DNA biopolymer with optimal light emission properties are of great interest.

In this paper, a comparison between the temporal evolutions of the transmittance and of the fluorescence emission of solutions and thin films of DNA – CTMA materials doped with the well-known luminophore Rhodamine 610, when they are illuminated with c.w. laser light at 532 nm wavelength, will be presented. In addition, the influence of the DNA – CTMA matrix on the temporal dependence of absorption changes induced by light at 532 nm will be discussed by comparing the results obtained for DNA – CTMA – Rhodamine 610 and for Rhodamine 610 solutions.

All the obtained results suggest that the proposed materials could be used in nonlinear photonics and for photonic functionalities based on light-emission (amplified spontaneous emission, lasing), in particular for dye-doped solid-state lasers.

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Electrochemically deposited organic layers as light-activated antimicrobial coatings

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Thin organic layers deposited on solid surfaces have been widely described in literature for application in organic electronics, biotechnology, or catalysis. Lately, layers containing organic photosensitizers are also extensively investigated e.g. for application in prevention of accumulation of pathogens on surfaces of daily-used objects. The main advantage of such photoactive layers is their remarkable biocidal efficiency that is related to the production of Reactive Oxygen Species (ROS) (Figure 1) [1]. ROS act in a highly effective and non-selective manner against microorganisms, which reduces the possibility of development of antimicrobial resistance [1,2]. The practical use of the light-activated antimicrobial coatings is still quite limited and the key constraints, like (photo)stability, long-term action and ease of the deposition procedure, have yet to be overcome.

In our work, the photoactive coatings based on phenothiazine or phthalocyanine derivatives have been deposited in an electrochemical process. The influence of chemical structure and morphology of the layer on its photoactivity has been investigated. Finally, the antimicrobial response were examined against selected bacterial strains.

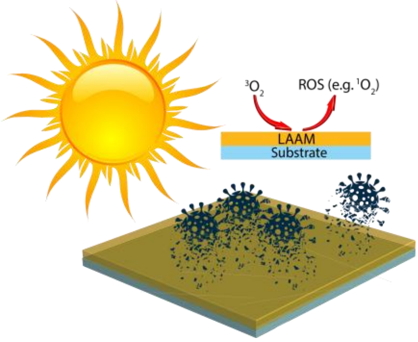

Figure 1: General scheme of action of light-activated antimicrobial coatings (LAAM)

The work was financially support by EU under Horizon 2020 program
(OCTA project, grant agreement No. 778158).

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Studies of the Polymerization Process of Branched Polymers Based on Monte Carlo Simulations

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A simple model was developed for studies of the polymerization process of branched polymers. Monte Carlo simulations were carried out by means of Dynamic Lattice Liquid algorithm [1]. A living polymerization in bulk of dendrimers, hyperbranched polymers, and star-branched polymers was studied. A core-first methodology was used in a living polymerization of stars with up to 32 arms, and hyperbranched polymers and dendrimers consisted of 4-functional segments [2-3]. The mass and structure of both types of macromolecules were studied. The influence of the functionality of well-defined cores on the structure of the system was also examined. The differences in the kinetics in the formation of the studied architectures, and changes to their structures were discussed.

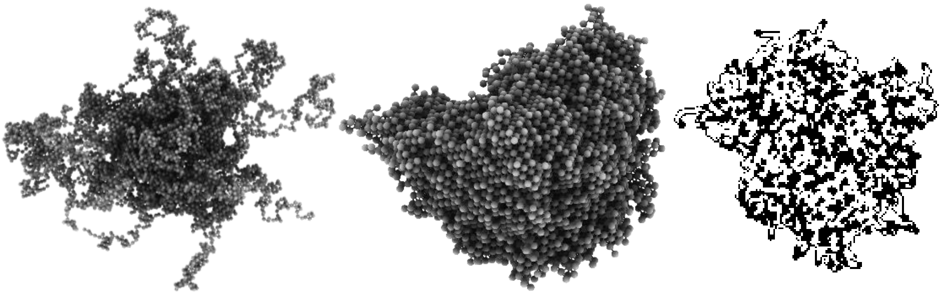

Figure 1: Typical conformations of stars, dendrimers and hyperbranched polymers.

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Sustainability scenarios across the lifecycle of emulsion polymers

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Trinseo is a company focusing particularly on the manufacture of plastics and emulsion polymer binders. Beyond traditional polymers, Trinseo's sustainable product portfolio offers alternative solutions to help customers achieve their sustainability goals.

As demand for sustainable products continues to increase, and new government regulations for a net zero future are put into place, the materials and manufacturing industries need to accelerate their transition to sustainable resources. This requires us to reimagine our materials' composition, their use, and their disposal as well as diversify our feedstocks sources to non-fossil in order to transition to net zero emissions.

Our emulsion polymers (Latex Binders) portfolio features innovative, materials solutions for applications that touch lives daily in coatings, adhesives, sealants, and elastomers (CASE); paper and board; and textiles. Supported by more than seven decades of expertise, our comprehensive portfolio of binders solutions feature chemistries based on styrene butadiene and styrene acrylic, all acrylic, and vinyl acrylic latex.

We adopt a scientific approach as we develop products, continuously invest in recycling technologies, innovation and scientific tools such as LCA automation, Product Carbon Footprint calculations and reporting, mass balance, blockchain, and more. Additionally various other approaches to sustainability of the product will be presented like bio-based, post-consumer recycled and pre-consumer recycled containing, low VOC raw materials.

IL9

Polymer nanocomposites for industrial applications: challenges and opportunities

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Polymer composites are regularly used in the electrification devices. Their appropriate functionality is crucial for ensuring the proper operation of electrical devices. Several applications of polymer nano- and micro-composites will be presented.

Firstly, the appropriate selection of the filler and the processing methods will be discussed, in order to prepare the polymer composite with desired properties. For example, to increase thermal conductivity in polymer composites the conductive paths must be maximized. Hence, one should select the most suitable filler and processing method that will lead to a composite with an appropriate thermal conductive functionality. For this reason, the modification of the filler materials can give a promising solution. An approach will be discussed related to use of the graphene nanoplatelets based hybrid filler for the thermal conductivity enhancement in the epoxy resin based composites [1].

Then, a method to enhance the gas–barrier properties of polymers will be discussed, as polymers are used in gas insulated electrical apparatuses. Polymeric materials gradually replace conventionally used metals and thermosetting resins thanks to the easiness of their processing, lightweight, low costs as well as multifunctional characteristics. However, these applications are often limited because of relatively high permeability for gases. This contribution will report on the gas barrier properties of the low density polyethylene based composites filled with different amounts of graphene nanoplatelets [2].

Finally, application of the shape memory polymers in the electrification devices will be presented. Shape memory polymers are commonly used for an application as the heat shrinkable electrical insulation components, e.g. heat shrink sleeves for cable joints, or simple shrinkable tubes for cables. Due to the flow of the electrical current through electrification components, as in cables and busbars, the additional heat is generated, which can lead to malfunctioning or even the damaging of the electrical devices. Therefore, suitable thermal management in order to dissipate the excess of generated heat is a crucial issue for the appropriate functionality of electrical apparatuses [3].

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How thermosetting based materials could contribute to circular economy?

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Thermosetting materials like epoxy constitute a new type of waste source since these materials have appeared in many industrial applications with relatively long life spans such as structural composites for aeronautics or automotive, coating or isolating materials for electronic applications.

In this talk, different pathways will be described to show how these thermosetting polymers could contribute to the circular economy : i) The epoxy prepolymer was re-designed to be environmentally friendly while integrating the end of life : In this work, we have designed and engineered for the first time degradable multifunctional epoxy with a ionic liquid backbone [1] ; ii) The formulation of epoxy polymer was rethought by using clean process such as UV polymerization : cycloaliphatic epoxidized imidazolium ionic liquids were successfully synthesized with high yields and appear as promising candidates to replace bisphenol A derived polymers [2]; iii) The self-healing of epoxy materials can also be an alternative to the recycling by having the ability to heal the cracks and to prolong the life time: the synthesized microcapsules contained an epoxy resin able to act as a healing agent in presence of ionic liquid [3]. All these epoxy networks were deeply investigated in terms of thermal and mechanical properties, hydrophobicity, fire resistance and shape memory to be sure to develop high-performance environmentally friendly new epoxy materials for the continuous progress of a circular economy.

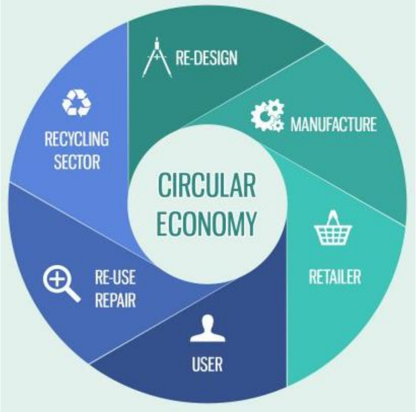

Figure 1: Different routes contributing to circular economy of polymer materials

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IL11

Multifunctional bionanocomposites based on lignin and its hybrids: use in packaging, biomedical and agriculture sectors

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The preparation of lignin based nanocomposites and its hybrid systems needs different blending procedures and chemical modifications. In its original state, lignin can enhance mechanical and thermal stability of a polymeric blend or a composite, acting as a UV blocker, antimicrobial, antioxidant agent. Lignin, as a natural three-dimensional network, has shown the ability to create uniform composite structures with inorganic nanoparticles, so organic–inorganic hybrid materials have similarly received wide-ranging attention. The production of lignin/inorganic hybrid nanosystems represents also a new methodology for high-value reuse of this material, since the hybridization potentially combines the benefits of all constituents to acquire matching synergic properties. Results related to the use of lignin nanoparticles (LNP) in a synergic role with metal oxides (MO) or as hybrids (MO@LNP) in polymeric matrices for food packaging, seeds priming or 3D porous scaffolds for cells growth or dye removal are discussed [1-3].

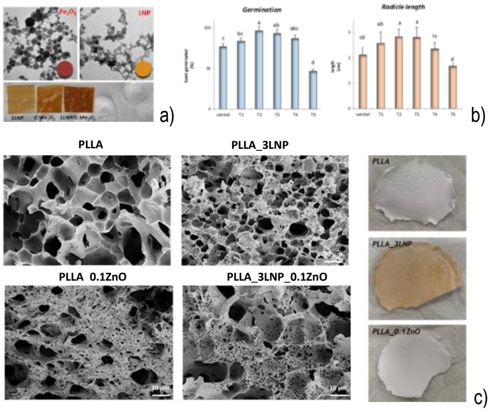

Figure 1: (a) TEM images for Fe_2O_3, LNP and visual images of PLLA films containing the two nanofillers); (b) effect of the treatments with ZnO@LNP on the shoot and root length and fresh weight compared to the untreated controls (T1, T2, T3, T4, and T5 refer to the ZnO@LNP concentration used for seed nano-priming); (c) PLLA based scaffolds obtained by TIPS in presence of LNP, ZnO and ZnO@LNP as function of dioxane/water ratio

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Carbazole dendrimers as efficient thermally activated delayed fluorescence and luminescent radical materials

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Carbazole dendrimers have a head-to-tail type molecular structure and unique polarized electronic structure with HOMO localized in the outer layer and LUMO localized in the inner layer [1]. This electronic structure matches the design principle of thermally activated delayed fluorescence (TADF) materials. TADF materials are attracting attention as third-generation OLED materials and we have reported the first solution processable TADF dendrimer based on the carbazole dendrimer donor[2]. TADF dendrimer can be utilized not only for OLEDs but also for LEC(light-emitting electrochemical cells) devices (Figure 1 left). We also found that carbazole dendrimerization is effective in improving the efficiency of doublet (radical) luminescent materials, which are fourth-generation OLED materials (Figure1 right)[4].

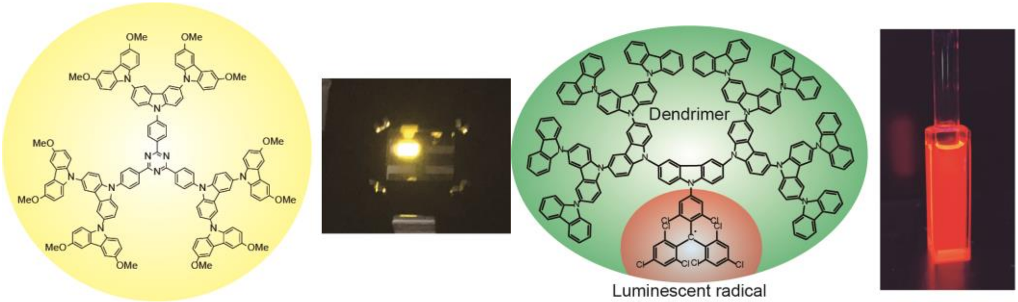

Figure 1: (Left) Structure of a TADF dendrimer and yellow emitting LEC device. (Right) Structure of 4th generation carbazole dendronized luminescent radical and the red emission in cyclohexane solution.

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Automated roll-to-roll manufacturing of printed Organic Photovoltaics through In-line Metrology

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Organic photovoltaics (OPVs) are a promising new technology for solar energy generation. They offer several advantages over traditional silicon solar cells, including low cost, light weight, and flexibility. However, the large-scale manufacturing of OPVs is still a challenge. Although there have been outstanding advances worldwide in the development of printed OPV materials and device architectures, their introduction to the market can only be realized when we achieve a sustainable, cost-effective, and reliable manufacturing process. To achieve this, we need to understand how the structural morphology and crystallization dynamics of organic semiconductor blends affect their optoelectronic and charge transport properties in multilayered device architectures.

In this presentation, we will discuss the innovations in automated manufacturing of flexible organic photovoltaics (OPVs) based on novel electron donors, such as PBDB-T and PPDT2FBT, and non-fullerene acceptors such as Y5 derivatives with better solubility in green solvents, in binary and ternary configurations. We will also provide an overview of the main factors that affect the optoelectronic performance and the large area homogeneity of these printed nanolayers on flexible substrates. Additionally, we will focus on how intelligent in-line metrology (optical, electronic, structural) can measure and analyze in real-time the nanoscale thickness, optoelectronic properties, and potential defects over large areas.[1] This approach will pave the way for the reliable large-scale manufacturing of flexible OPV devices with improved charge transport properties and performance, as well as significant device-to-device reproducibility. This will meet the requirements for the integration of OPVs in commercial applications in renewable energy generation, energy-efficient buildings, agrivoltaics, automotive, and transport, among others. [1,2]

[1] EU H2020 Project RealNano (www.realnano-project.eu)
[2] EU H2020 Project MUSICODE (www.musicode.eu)

Efficient single-layer blue organic light-emitting diodes

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It is generally accepted that for organic light-emitting diodes a multilayer structure is essential for obtaining a high efficiency for the conversion of current into light. A typical multilayer OLED consists of 5 or more organic layers, which serve to transport electrical charges to the emissive layer, in which charges and excitons are confined by additional blocking layers. As such, it is ensured that electrical charges are converted into photons as efficiently as possible. This concept has proven to be paramount for achieving high efficiency OLEDs over the last decades.

However, there are several drawbacks of such a multilayer architecture. First of all, many organic materials and deposition steps are required to fabricate such and OLED, which is costly and excludes the possibility of inkjet-printed OLEDs. Second, all layers and materials have to work in conjunction, to accomplish effective charge injection, charge transport, and charge and exciton confinement inside the emissive layer, which makes the design and material selection cumbersome. Third, the many heterojunctions in the device lead to voltage losses and may be potential sources of device degradation. And fourth, it is difficult to understand the device physics, since the many layers and heterojunctions introduce unknown parameters, such as barrier heights and charge transport properties, making the device analysis and optimization a trial-and-error process.

Here, we present highly simplified single-layer blue OLEDs based on thermally activated delayed fluorescence. The emissive layer is simply situated between two electrodes, providing direct charge injection. This extremely simple OLED exhibits an external quantum efficiency of 27.7%, equating to an internal quantum efficiency of unity, meaning that effectively all injected charges are converted into photons. This is achieved with a polymeric anode with a very high work function for efficient hole injection, and a low work function metal cathode for efficient electron injection. This device architecture is demonstrated to work even for a blue emitter, for which efficient charge injection and transport is notoriously difficult due to the high energy gap. The unity internal quantum efficiency proves that surrounding charge-transport and blocking layers, contrary to existing knowledge, are not required once efficient charge injection is ensured. In terms of efficiency, this single-layer OLED is on par with the best multilayer OLEDs.

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ORAL PRESENTATIONS

Triphenylene-tricarboxyamide based supramolecular polymers: from solution to surface studies

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Supramolecular polymers have attracted great attention because of their potential for the design of responsive materials with properties inaccessible to covalent polymers [1]. Supramolecular polymers are brought together through reversible and directional noncovalent interactions, leading to polymeric properties in solution and bulk states. Surprisingly, despite the great effort put on the development of new functional materials for optical or electronic applications, the strategy of utilization of cooperative supramolecular polymers has been rarely reported. One of the most studied synthetic supramolecular systems is based on benzene-1,3,5-tricarboxyamides (BTAs), which forms 1D helical fibers by combination of noncovalent interactions: threefold hydrogen bonds and π-π stacking. Despite extensive molecular engineering of the BTAs, their use as electro- and photo-active materials appears impractical, due to the small aromatic core.

To address this issue, we have recently developed a supramolecular motif based on a C_3-symmetrically substituted triphenylene core decorated with three amide groups, a triphenylene-2,6,10-tricarboxamide (TTA) [2]. Within this presentation the fabrication of helical supramolecular polymer (*p*TTA) fibers will be shown. Several parameters, including TTA (monomer) concentration and deposition method, will be discussed as the control means in obtaining fibers on surface. Apart from that, the results of the alternative, surface-promoted 2D self-assembly will be shown. The long-term goal of the presented work is the development of new functional materials for chiral optoelectronic applications.

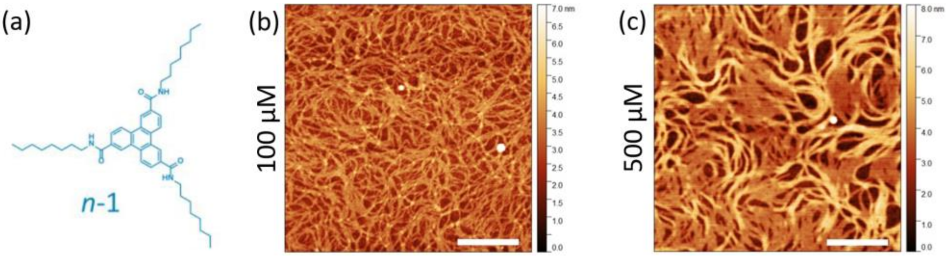

Figure 1: Structure of ***n*-1** TTA and the AFM images of *p*TTA supramolecular polymer fibers.

The project was carried out within the International Research Agendas PLUS program of the Foundation for Polish Science, and was co-financed by the European Union under the European Regional Development Found (MAB PLUS/2019/11).

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Micromechanisms of plastic deformation of semicrystalline polymers studied by positron annihilation lifetime spectroscopy (PALS)

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Annually, over 350 million tons of polymers are synthesized, most of which are semicrystalline. The specific physical properties of semicrystalline polymers are derivative of their unique micro-/nanostructure. The presence of lamellar crystals and amorphous layers determines the properties of semicrystalline polymers and affects the process of their deformation. Although a number of investigations on plastic deformation of such materials, important areas remain poorly understood, especially regarding the role of the amorphous component. Small angle X-ray scattering (SAXS) technique is usually used to analyze the initial stages of deformation of semicrystalline polymers. However, this technique allows the detection of objects whose size ranges from several to several dozens of nanometers. Meanwhile, the initial size of free volume pores of the amorphous phase remains within 0.1-0.15 nm^3 [1]. One of the most valuable tools enabling the direct analysis of the size/distribution of free volume pores of the amorphous phase and characteristic free spaces of the crystalline component is the positron annihilation lifetime spectroscopy (PALS).

In the work PALS was used to track the deformation-induced changes of the structure of the amorphous component of semicrystalline polymers. The studies, after appropriate adaptation of the PALS technique in accordance with the methodology presented in our works [2,3], were carried out from undeformed samples to stretched slightly after a yield point at stress/strain curve. Based on the results of the mean o-positronium lifetime (τ_3), it was indicated that the average size of the free volume pores of the amorphous phase in the studied strain range rather decreased in comparison with the undeformed polymer, even after the initiation of the cavitation. It was also shown that the cavitation phenomenon was responsible for the increase of the dispersion of o-positronium lifetime (σ_3).

The studies were financed from funds of the National Science Centre on the basis of the decisions number DEC- 2018/30/E/ST8/00364.

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Additive manufacturing of self-monitoring biobased SWCNT loaded resin

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A self-monitoring material is a material capable of detecting its own deformation status without using an external sensor thanks to piezoresistivity. This effect is primarily present in polymer-matrix composite materials filled with an electrically conductive filler (i.e. single walled carbon nanotubes SWCNT). When a composite system with a percolating network of conductive particles is subjected to mechanical deformation, a variation in the overall electrical resistance is measured [1]. High-performance sectors such as aerospace, bio-medical and automotive are clearly the perfect application for self-monitoring materials especially when this materials are processed by additive manufacturing which allows for the production of components with complex geometry and short lead-time. On the other hand, in the last years always more attention is paid to sustainability focusing on the production of new sustainable materials coming from natural sources. In this perspective, biopolymers derived from vegetable oils (i.e. soybean oil) could be a good alternative to synthetic polymers derived from petroleum oil to realize self-monitoring 3D printable components [2].

In this work biobased resins mainly composed of acrylated epoxidized soybean oil (AESO) loaded with 0.25 wt% of SWCNT were produced and 3D printed with the DLP 3D-printing process in order to obtain self-monitoring structures. The CNT addition plays a role in the curing process due to the CNTs UV absorption which is compensated by increasing the exposure time. The 3D printed samples show good dimensional accuracy and a low degree of shrinkage. FTIR, swelling and density analysis suggests that the CNT loaded samples present a slightly lower crosslink density caused by the nanofiller presence. The CNT-loaded samples present a piezoresistive behavior, displaying a variation of electrical resistance with the application of load, proving strain-sensing and self-monitoring capabilities. Moreover accelerated degradation tests proved that 3D printed resins are bio-degradable by hydrolytic mechanism.

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Understanding the role of molecular interactions in the emission of two ESIPT isomers for thin film applications

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Excited state intramolecular proton transfer (ESIPT) molecules have demonstrated unique properties of light emission including a large Stokes shift. The molecular interactions in ESIPT materials determine their emission properties, but also impact other common characteristics such as reactivity, molecular energy levels or molecular packing. Although thin film optoelectronics is considered as a potential application of ESIPT dyes, their study is normally focused on solution and/or bulky solid states. However, insights about ESIPT materials in thin films are highly required.

The study of two new ESIPT isomers revealed that the molecular interactions impacted by the different molecular geometry strongly affect their properties in solution and thin films. Moreover, parameters like the emission bandwidth and fluorescence quantum yield (QY) of the films could be modified by the choice of solvent for spin-coating or by thermal annealing. Such tuning was found to be closely related to the intermolecular interactions within the deposited materials, as demonstrated by the spectroscopic and morphological analysis of the thin films. The combination of suitable thermal annealing and solvent selection provided a strategy to increase the QY of the films of up to 150%, which opens a new route for the optimization of ESIPT materials emission and their applications.

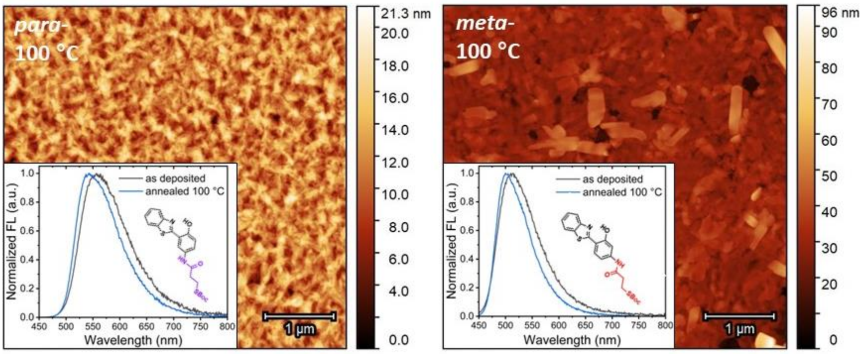

Figure 1: AFM images and fluorescence spectra of the two ESIPT isomers studied.

The project was carried out within the International Research Agendas PLUS program of the Foundation for Polish Science, and was co-financed by the European Union under the European Regional Development Found (MAB PLUS/2019/11).

Oligo(ethylene glycol) methyl ether methacrylate based hydrogel with intrinsic antimicrobial activity against *Pseudomonas aeruginosa* as a model of a major wound infecting human pathogen

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A novel and easy-to-handle wound dressing material based on the well-defined copolymers of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) is presented. The discussed material was perfectly biocompatible with human dermal fibroblasts and revealed an auspicious degree of intrinsic antibacterial activity against *Pseudomonas aeruginosa* as a model pathogen for hospital-acquired infections. Formation of bacterial biofilms was prevented in early- and late-stages and even planktonic cells were killed upon gel contact. The rheological properties of the hydrogel materials were comprehensively characterized in both dry and swollen states. Excellent biological performance and appropriate viscoelastic properties qualify the hydrogels as promising novel wound dressing materials with contact-active bactericidal activities.

The financial support from National Science Centre, Poland is gratefully acknowledged (Grant UMO-2020/39/I/ST5/02108).

Application of Hydrogels for Wine Acidity Control

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Spain is a prominent wine-producing country, with a total production of 33 million hL in 2022, and Castilla-La Mancha being the main wine region [1]. Wine acidity management has become a concern, especially in warm regions experiencing low acidity, which is now spreading to other areas with less extreme climates [2]. Acidity plays a vital role in microbiological stability, color preservation, and sensory properties of wine.

Various technologies have been developed to address wine acidification and pH reduction. The primary methods employed currently involve the addition of tartaric acid and the use of cation exchange resins, although the latter results in the loss of phenolic compounds and aromas [2]. Therefore, minimizing the loss of these compounds has become a significant challenge.

Hydrogels are three-dimensional cross-linked polymers with diverse properties [3]. To respond to pH stimuli, hydrogels require polymers containing pendant acidic or basic groups that can accept or donate protons.

The objective of this research was to evaluate the application of two hydrogels synthesized from maleic and hyaluronic acids, respectively, on red and white wines. The aim was to lower the pH to desired levels while minimizing negative effects on phenolic composition and sensory characteristics, particularly color.

Preliminary results indicate that both hydrogels effectively lower the initial pH of red and white wines while maintaining their phenolic composition. No changes in the color parameters of red wine were observed, while slight changes were found in white wine, though statistically insignificant. Based on these findings, the application of these hydrogels could be proposed as a new effective method for acidification in wines.

We would like to acknowledge the support and funding provided by IRICA (UCLM) for the HydrowinepH project.

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OR7

Understanding Degradability of Vinyl Polymer Networks with Cleavable Strands or Crosslinks

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Designing degradable or re-processable polymer networks, such as thermosets or elastomers is a formidable challenge due to their crosslinked structure. Among them, networks based on vinyl polymers such as polyacrylates, or polystyrene are particularly challenging as they contain exclusively carbon-carbon backbones.

Using crosslinkers with cleavable groups (e.g., disulfides) seems like a straightforward method to develop fully degradable vinyl polymer networks. However, networks/gels prepared by conventional free radical polymerization (FRP) typically cannot be degraded even when they contain cleavable crosslinkers. This is due to their extremely complex internal structure and formation of dense clusters (microgels) during crosslinking.

I will present the recent work in our group focused on enabling degradability of polyacrylate networks by incorporating dibenzo[c,e]oxepane-5-thione (DOT) in the backbone (strands) using radical ring opening polymerization (rROP) under conventional or controlled polymerization conditions, followed by reduction of the formed C-S bonds (Figure 1) [1]. Additionally, I will discuss our attempts to better understand (non)degradability of networks/gels prepared from different classes of vinyl monomers, that is (meth)acrylates, acrylamides, and styrene, by analyzing their polymerization kinetics and the resulting network topologies.

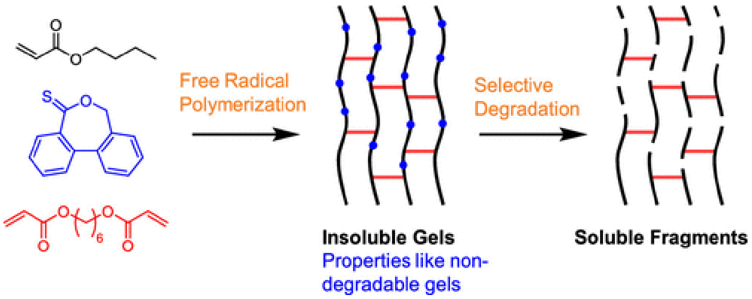

Figure 1: Schematic illustration of synthesis and degradation of poly(*n*-butyl acrylate) networks with cleavable sites by incorporation of DOT in the network strands.

Acknowledgments: RSC Research Enablement Grant E21-2719779284; EPSRC New Investigator Award EP/W034778/1.

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Spherical and spheroidal poly(D,L-lactide-co-glycolide) particles: preparation and studies of degradation in vitro

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Biodegradable microspheres prepared from various copolymers are commonly used in drug delivery systems as the biologically active agent carriers. However, the knowledge on carriers with shape anisotropy is still very scarce. Moreover, understanding of the mechanism of particles degradation is not well understood. The aim of our study was explanation of degradation process of spherical and spheroidal particles and finding relations between particles shape and degradation mechanism at physiological conditions in vitro. The particles were prepared from poly(D,L-lactide-co-glycolide, PGLA) (Resomer® RG504H) in water by classical nanoprecipitation method using poly(vinyl alcohol) (PVA) as emulsifier. The spherical particles with ,$_n$=3.2 μm and dispersity factor equal 1.3 were obtained. The PGLA microspheres embedded in PVA film underwent deformation into prolate spheroids in Instron tensile test system at 90 °C in controlled conditions of stretching, above T_g of both, polymer forming matrix and particles. The spheroidal particles with aspect ratio (AR) in the range 2-7 were obtained. The progress of particles degradation in aqueous environment (pH=7.4, 0.02 M, T=37.0 ±0.5 °C) was monitored using AFM, SEM, GPC and gravimetric analysis. The results of the studies revealed differences in time and mechanism of particles degradation related to particles native shape. For example, spheroid degradation preceded particle swelling leading to a change of their shape to spherical one and delayed degradation (see Figure 1a,b).

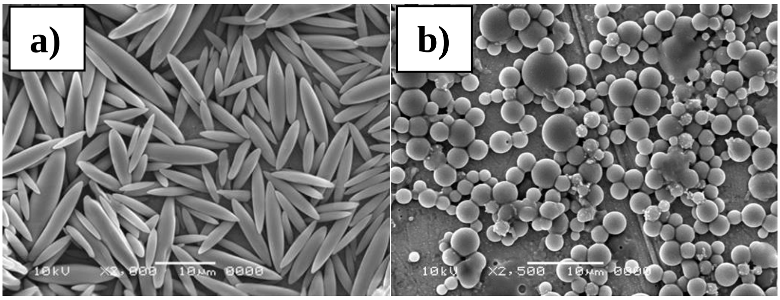

Figure 1a,b: PGLA spheroids with AR=4.85 before and after 4 weeks of degradation at 37 °C.

Acknowledgements: The authors express their gratitude for financial support from National Science Centre (Poland) grant Nr UMO-2018/29/B/ST8/01721.

New Epoxy-Ionic Liquids Networks as Matrices of Carbon Fiber-Based Composites of Type IV Hydrogen Pressure Vessel

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Compact, reliable, safe, and cost-effective storage of gaseous hydrogen under 700 bar is a key challenge to the widespread commercialization of fuel cell electric vehicles (FCEVs) and other fuel cell applications. The objectives of this research focus on the chemistry of fast curable epoxy system used as matrix of the composite part of type IV H_2 vessels leading to compliance with the many specifications required for the final composite material. In fact, the carbon fiber-based composite material is processed directly on the liner part of the vessel (usually HDPE of polyamide). According to the nature of the material liner, long curing times at limited acceptable temperatures, are required.

Ionic Liquids (ILs) have been reported as new alternatives of conventional hardeners such as diamines or anhydrides, of reactive epoxy systems as well as for improving performances of epoxy networks including their application to fiber-based composite materials [1,2]. Especially, the influence of ILs on the reaction kinetics of epoxy reactive systems was reported as the way to tailor the reaction time allowing the design of epoxy systems from fast curable to conventional ones. Thus, the aim of this work is to study the reaction mechanisms and kinetics of the polymerization of epoxy resins in the presence of ionic liquids. Based on such a knowledge, it is possible to control, *i.e.* to increase their reactivity compared to conventional formulations, and to propose new fast curable resins for composite materials used as high-pressure storage hydrogen tanks. A new generation of epoxy networks having a glass transition temperature ranging from 90 to 150°C, a good thermo-mechanical and mechanical properties, a hydrophobic behavior, and corrosion protection have been developed.

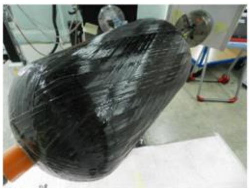

Figure 1: First generation of epoxy-IL formulations applied for processing Hydrogen Composite Pressure Vessel

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SAXS/WAXS mapping of nanostructured polymers: from image to nanostructure

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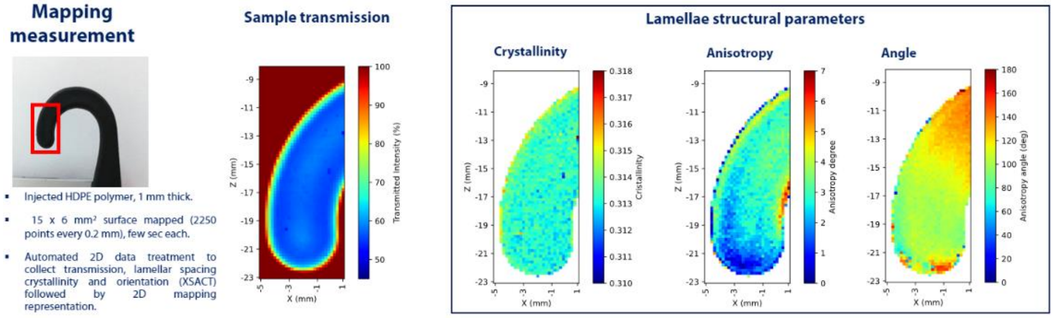
The characterization of polymer materials typically involves the combination of multiple techniques, including microscopy, elemental analysis and mechanical testing. We introduce a novel approach that combines imaging and nanostructure characterization, which is for the first time accessible in a practical manner at the laboratory scale. This innovation expands the range of length scales that can be investigated using small angle X-ray scattering (SAXS) from Ångströms to millimeters. The integration of SAXS and radiography analysis provides valuable insights into the relationship between macrostructural heterogeneities and the nano- or atomic structure of heterogeneous samples. In addition, we present newly developed measuring configurations available on modern SAXS/WAXS laboratory instrument: a focused incident beam channel for mapping polymers atomic and nanoscale structure and an X-ray rimaging module. Those motorized set-ups offer rapid and automated switching between traditional X-ray scattering measurements in a mm^2 probed area and X-ray radiography or X-ray mapping measuring channel.

While the mapping of polymers using a micron-sized beam has been developed at 3rd generation synchrotrons over the past two decades, such measurements have been limited in laboratory set-ups due to the reduced flux of X-ray sources. This limitation has resulted in either small inspection areas of a few mm^2 or excessively long experimental times spanning a few days. By utilizing short focus optics and compact collimation, we demonstrate the capability to map and automatically extract nanostructural parameters of the examined polymer at each inspected point within a few seconds.



- Injected HDPE polymer, 1 mm thick.
- 15 x 6 mm² surface mapped (2250 points every 0.2 mm), few sec each.
- Automated 2D data treatment to collect transmission, lamellar spacing crystallinity and orientation (XSACT) followed by 2D mapping representation.

Figure 1 Combined imaging and nanostructure characterization of injected HDPE polymer showcasing the experimental details, the sample transmission and false-color maps that depict the distribution of various lamellae structural parameters across an area of approximately 100 mm^2.

To illustrate this technique, we present the analysis of a typical injected HDPE (high-density polyethylene). We generate false-color maps that depict the distribution of crystallinity, lamellar spacing, degree of lamellar orientation and the primary orientation of the lamellae across an area of approximately 100 mm^2 within an hour (Figure 1). This advancement holds significant potential, as the increased X-ray flux density allows for fast post-processing material analysis or to conduct operando measurements at lab scale time resolutions. The set-up also provides significant gain in grazing incidence configuration for thin film analysis.

To highlight the advantages of integrating X-ray imaging together with SAXS, we present a combined scattering and imaging analysis of composite samples used to detect manufacturing defects. Furthermore, we also showcase measurements conducted on polymer films subjected to strain, where X-ray transmission imaging is employed during a tensile test to identify specific points of interest within the sample (Figure 2). The variations between the subsequent local scattering measurements are thus put into context and explained by the imaging.

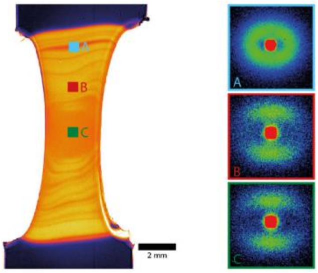


Figure 2: X-ray transmission imaging performed during a tensile test and associated local scattering measurements of selected points of interest.

Latest developments in atomic force microscopy for polymer research

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The atomic force microscope (AFM) has become a true enabling platform for the visualization and probing of polymeric materials at the nanoscale. Importantly, AFM measurements can be carried out under the relevant experimental conditions including ambient, gaseous or liquid environments over a wide range of temperatures. In addition to nanoscale topographical information of polymers the mapping of the respective physical and chemical properties has witnessed mayor technological breakthroughs over the past decade.

Here we present a selection of recent highlights and breakthroughs with respect to the quantitative mechanical, electrical and chemical probing of polymers at the nanoscale.

Latest developments in nanomechanical property mapping of polymers include modes such as PeakForce QNM [1] or contact resonance, to identify material variations unambiguously and at high spatial resolution. We introduce atomic force microscopy nanoscale dynamic mechanical analysis (AFM-nDMA), a new mode for quantitative viscoelastic analysis of heterogeneous polymer materials [2].

A variety of AFM based nanoelectrical property mapping modes became available in recent years including PeakForce TUNA [3] and DataCube modes [4]. By correlating mechanical and electrical data a deeper understanding of the polymer surface properties is gained.

One method of nanoscale infrared spectroscopy and imaging, atomic force microscope based infrared spectroscopy (AFM-IR) directly detects IR radiation absorbed by the sample using the AFM probe tip to sense thermal expansion. This thermal expansion depends primarily on the absorption coefficient of the sample and is largely independent of other optical properties of the AFM tip and the sample.

Over the last years, we have developed two major improvements in the photothermal AFM-IR technique and introduced [5] resonance enhanced version of AFM-IR and [6] Tapping photothermal-based AFM-IR spectroscopy and imaging. Recently, building on our knowledge in photothermal AFM-IR, we have invented the surface sensitive AFM-IR mode. This mode allows to chemically analyze sample surfaces with a high degree of surface sensitivity by measuring IR spectra and/or images of the top of the sample surfaces.

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The DLL (Dynamic Lattice Liquid) model. How it works?

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The dynamic lattice liquid (DLL) model at the first time was proposed in the late 90's of the 20th [1]. This lattice model basing on the concept of a strictly cooperative motion of molecules makes it possible to study molecular dynamic with full and easy control of mobilities of various species on the microscopic level. Moreover, the DLL model properties are in good agreement with dynamical properties of liquids [1]. It is worth emphasizing that, contrary to many other models, DLL offers the possibility of investigations of the systems with the density factor $\rho = 1$ (i.e. with all occupied lattice sites). As depicted in Fig. 1, the cooperative rearrangements on the lattice have a form of closed loops of displacements of at least three molecules. A triangular lattice with periodic boundary conditions is employed in the performed simulations. Time is assumed to be a discrete variable and positions of all molecules are updated simultaneously (algorithm based on DLL model is strictly parallel). At any moment each lattice node is occupied by exactly one molecule, and a unit vector $\mathbf{v}_k$ is assigned to each molecule k that poining randomly at one of the nearest neighbor sites. This vector represents the direction along which the molecule attempts to jump to an adjacent site. The molecules that do not belong to a closed loop are immobilized at this time step, the rest ones move within the closed loops. Next, a new vector field $\{\mathbf{v}_k\}$is randomly assigned to the molecules, and the described procedure starts again. As an example of an issue illustrating the operation of the DLL algorithm, a simulation of the aggregation process was selected.

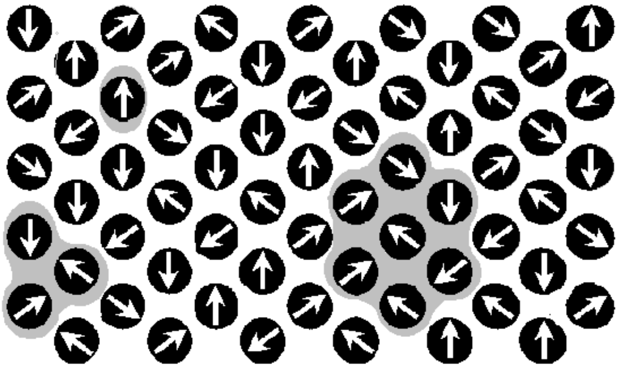

Figure 1: An example of the vector field that defines directions of attempted molecular displacements toward neighboring lattice sites in the DLL model. Shadowed groups represent closed loops of at least 3 molecules; only displacements in these groups will actually take place.

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Approach to fully solution-processed organic electronics- role of interlayers

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Inks commonly used for deposition of electrodes by inkjet printing method contain suspension of silver or, more expensive, gold nanoparticles in polar solvents. However, the standard work functions of silver, which is in the range of 4.26 – 4.74 eV or chemically derived graphene, which is in the range of 4.20 – 4.60 eV, are not well suited for making electric contacts to typical organic semiconductors. One strategy towards that is to develop methods for modifying the effective work function of standard and convenient electrode materials, such as silver, ITO and graphene electrode. Such a modification can take place by introducing a monolayer or extremely thin interlayer (< 10 nm) of an organic or inorganic modifier on the surface of the electrode. The interlayer mechanism of operation can be different and it depends on the type of device.

The presentation will cover examples of interlayers that have been successfully applied to OLEDs, OPVs and photodiodes, allowing them to achieve high luminance (8,000 cd/m2) for OLEDS with printed interlayers and PCE for PV at the level of 17%, respectively.

This work was financially supported by the National Centre for Research and Development (NCBR Poland) under grant POLBER/5/63/PrintedQDD/2022.

Optimized Charge Transport in Molecular Semiconductors by Control of Fluid Dynamics and Crystallization in Meniscus-Guided Coating

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Solution processable organic semiconductors (OSCs) hold advantages for the fabrication of flexible and large-area electronic devices. Control over morphology and molecular packing of OSCs is crucial to realize excellent charge carrier transport in organic field-effect transistors (OFET). Meniscus-guided coating (MGC) methods, such as zone casting, dip coating and solution shearing, are scalable laboratory models for large-area solution coating of functional materials for thin-film electronics. Unfortunately, the general lack of understanding of how the coating parameters affect the dry-film morphology upholds trial-and-error experimentation and delays lab-to-fab translation.

In this combined experimental and modelling study, we present a predictive model for structure formation upon crystallization of a (generic) molecular semiconductor during MGC, driven by solvent evaporation. Predicted surface morphologies are fully reproducible by an experimental data which show correlation between coating speed, domain growth, long-range alignment, and charge carrier transport.[1,2] With increasing casting speed, we identified three morphological subregimes; I) an isotropic domain-like structure, II) a band-like structure following the coating direction and III) a corrugated morphology lacking directionality[3].

We interpret our experiments using numerical simulations of the steady state fluid dynamics in the bead and the morphology formation in the deposited film, focusing on the onset of the appearance of unidirectionality. We reveal a direct correlation between the trap density in the OSC film and the casting speed and show how this allows us to achieve an improved saturation and effective charge carrier mobility, with a high reliability factor. The found correlations are crucial for the development of MGC as a practical processing technique for upscaling the solution deposition of organic semiconductors in future.

T.M. acknowledges the Foundation for Polish Science financed by the European Union under the European Regional Development Fund (POIR.04.04.00-00-3ED8/17).

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Conductive polymer composites for heating and sensor applications in vehicle structural components

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As part of our project to develop flexible hybrid organic-inorganic electronics for vehicle structures and interiors, we investigated the dielectric properties of thermoplastic polyurethane (TPU) composites loaded with expandable graphite (EG) [1]. The composites were prepared by melt mixing and then compressed into discs for impedance spectroscopy (IS) analysis.

We examined the dielectric properties in relation to filler concentration (0 to 10 wt.%), frequency (10^{-2} Hz to 3×10^{9} Hz), and temperature (-30 °C to 120 °C) using IS, and correlated them with the material's morphology. We described the electrical behavior at the interface between the matrix and filler, particularly below the percolation concentration (c_p), and studied the influence of humidity. The dielectric constant (ε') of the polyurethanes was found to be around 6-7, which is higher than the average for insulating polymers (2-4) with few exceptions [2]. With 4 wt.% EG, just before reaching the c_p, ε' reached values of 16-18. The electrical conductivity (σ') decreased below the percolation concentration due to polarization effects at the matrix-filler interface, acting as electron traps. However, after reaching a minimum, σ' increased as the concentration of EG increased, following the percolation theory. Humidity was found to increase both σ' and ε', while suppressing polarization at the electrodes. Other phenomena, such as relaxations, were not significantly affected by the presence of water.

Based on the results obtained, TPU-EG composites can serve as excellent dielectric or conductive layers depending on the concentration of EG. However, these materials have limitations, such as their miniaturization potential, which is closely tied to the dimensions of the graphite nanoflakes, whose length can vary in the order of 10-100 μm. Another limitation is the hygroscopic nature of polyurethane, which can affect the electrical response. Nevertheless, this issue can be addressed through appropriate sealing techniques.

The authors wish to thanks Technology Agency of the Czech Republic TAČR the financial support to the FEIM project (No. DP-TN02000067-001_Printed Electronics) and Ms Hana Vaňasova for the valuable technical work.

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Electrochemically tailored conjugated polymers as materials for electrochromic windows and OLED emitters.

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The OLED worldwide market is growing rapidly, and Europe needs experts with comprehensive knowledge and practical experience in this technology. OLED technology is used in small devices such as smartphones, tablets, and high-end TVs and lighting, as OLEDs are still relatively expensive compared to LCDs. But with research progressing towards lower cost and longer lifetime, together with a growing trend to use flexible displays in smartphones etc., the OLED market is growing fast. The organic light-emitting diodes (OLED) industry is very demanding in its search for new compounds that could be used as emitter material or in transporting layers. The OLED devices are typically divided into fluorescence and phosphorescence devices. Fluorescence is a fast relaxation process, where the excited molecule in the excited singlet state returns to the ground state by emitting energy in the form of photons. In fluorescent OLEDs, emission arises from the only radiative decay of singlet excitons, are radiative triplet exciton decay is forbidden. Therefore, the quantum efficiency of a fluorescent emitter-based device will be limited to 25%, which means that the 75% triplet excitons will be lost. To increase the efficiency of devices, it is possible to link fluorescence and phosphorescence and get 100% efficiency by employing the TADF process. In this new type of delayed fluorescence emitters, harvesting both singlet and triplet excited states to give 100% internal charge conversion into light allowed the possibility to replace very expensive Ir-based phosphors in OLEDs.

Here, we present an electrochemical and spectroelectrochemical investigation of three novel donor-acceptor-donor (D-A-D) materials comprising two diphenylamine (DPA) or modified DPA donors bonded to a single xanthone acceptor. Although a xanthone acceptor D-A-D derivative has been previously synthesised and used as a TADF material with limited success, as well as used as a sky blue triplet harvester within a FRET-based electroluminescence device, these materials have been synthesised explicitly for electropolymerisation to highlight a new design pathway for the creation of TADF polymeric materials.

InP-based Quantum Dots in Light Emitting Diodes: Connectivity of Device Performance and Surface Chemistry

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Technologically important, environmentally friendly InP quantum dots (QDs) typically used as green and red emitters in display devices can achieve exceptional photoluminescence quantum yields (PL QYs) of near-unity (95-100%) when the-state-of-the-art core/shell heterostructure of the ZnSe inner/ZnS outer shell is elaborately applied. [1] Nevertheless, it has only led to a few industrial applications as QD liquid crystal display (QD–LCD) which is applied to blue backlight units, even though QDs have a lot of possibilities that able to realize industrially feasible applications, such as QD light-emitting diodes (QD–LEDs) and luminescence solar concentrator (LSC), due to their functionalizable characteristics. [2]. In many cases, researchers expect the optical- and physical properties of electroluminescence devices to depend on the corresponding material's properties. Herein, we suggest an appropriate example to be able to elucidate why device performance should be considered independently from QD material side. Beyond the generation of highly emissive InP QDs with high color purity, this study mainly deals with the connectivity between QD materials and QD devices not only to make it a vital jumping-off for industrially feasible applications but also to reveal from chemical and physical standpoints the origin that obstructs the improvement of device performance experimentally and theoretically.

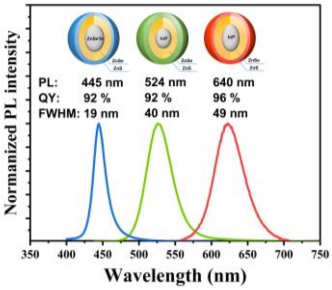

Figure 1: PL spectra of Cd-free ZnTeSe (blue) and InP (green, red) QDs

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PMMA as blend partner in PA6/carbon nanotube composite: Effect on morphology, rheology, and thermoelectric properties

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Starting from a study on polyamide 6 (PA6) nanocomposites with single-walled carbon nanotubes (SWCNTs), the effect of adding a second polymer, namely polymethyl methacrylate (PMMA), which is immiscible with PA6, was investigated [1]. The effect of PMMA content (up to 50 wt%) on the morphology and properties of unfilled blends and blends filled with 3 wt% SWCNTs was studied, with the blend composites prepared by small-scale melt mixing. The study includes scanning electron microscopy (SEM), optical microscopy (OM), rheological properties of the melt, electrical and thermoelectric properties. The morphology types are matrix-disperse particle morphologies at low contents and co-continuous morphologies at higher PMMA contents, with SWCNTs preferentially localized in PA6. SWCNTs refine the morphology and enhance the morphology stability.

The melt rheological investigation shows that corresponding to the strongly increased viscosity after filling PA6 with SWCNTs, the blends with SWCNTs also show significantly higher viscosity values than the unfilled blends. The convergence or excess of viscosity values of PA6/PMMA =50/50 wt% blends with SWCNTs compared to those of PA6 filled with 3 wt% SWCNTs from 1.5 wt% SWCNT addition indicates the formation of a co-continuous type of morphology, which is clearly visible in SEM and even OM images. This type of morphology is retained even after the extruded material has been compression moulded into sheets.

Regarding the thermoelectric properties, all composites and blends show n-type behaviour with negative Seebeck coefficients. By varying the blend composition, an increase in the absolute Seebeck coefficient, power factor (PF) and figure of merit (ZT) was achieved compared to the PA6 composite, mainly due to the selective localisation and accumulation of SWCNTs in PA6 at constant SWCNT loading. The maximum PFs achieved were 0.13 microW/m·K^2 for PA6/PMMA/SWCNT 60/40/3 wt% compared to 0.09 microW/m·K^2 for PA6/3 wt% SWCNT, an increase to 144%.

The authors thank the ERASMUS+ Mobility program for financial support of Mrs. Alice Liguoro (Université de Bretagne-Sud, France) and Mrs. Manuela Heber (IPF) for taking the SEM images as well as the collaborators of the IPF research technology department for their support in designing and building the thermoelectric equipment including the software.

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Controlling the morphology of thin layers of crystalline organic semiconductors

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Organic electronic devices are typically multi-layer structures composed of thin or ultra-thin layers. The morphology of individual layers has a decisive influence on the performance of these devices [1]. When materials are processed from solutions, the processes of crystal nucleation and growth can be controlled by the appropriate selection of various parameters, such as the type of substrate, type of solvent, solution concentration, temperature, evaporation rate or viscosity of the medium. This allows to obtain the continuity of the crystalline network, e.g. using the reticulate doping method [2], as well as highly ordered and anisotropic structures using the zone-casting method [3].

The crystallization process is much more difficult to control when the layers are produced by vapor deposition in a vacuum, because there are far fewer parameters to tune. Most often, the surface energy of the substrate is modified, because it determines whether the interactions between the deposited molecules are stronger, similar or weaker than those between the molecules and the surface, and it is assumed that consequently the crystallization process will follow the Volmer-Weber (VW), Stranski-Krastanov (SK) or Frank-Van der Merwe (FM) mode.

We have shown that after adding a very small amount (< 1 wt%) of TiO_2-containing hybrid nanoparticles to the polymethyl methacrylate (PMMA) used as a substrate, even a ultrathin (< 10 nm) layer of well-known semiconductor (C8-BTBT) deposited in a vacuum is continuous. This is impossible when the substrate is pure PMMA, which proves that the addition of TiO_2 nanoparticles changes the crystallization mechanism from the VM mode to the SK mode, although the surface energy of the substrate remains practically the same. We found that the addition of TiO_2 nanoparticles creates protruding spikes on the PMMA surface that facilitate heterogeneous nucleation and the formation of multiple crystalline domains of the semiconductor. The density of the nucleation centers increases with increasing TiO_2 content, which makes it possible to obtain very thin and continuous semiconductor layers, which were used to build functional field-effect transistors [4].

Acknowledgements: This work was supported by NSC, Poland, grant UMO-2014/14/A/ST5/00204.

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POSTER PRESENTATIONS

Tailoring the properties of ZnO through doping using simple wet chemistry methods

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Zinc oxide is an intensively investigated material due to its promising application in many fields, e.g. in optoelectronic devices, where it can play various roles. The most prominent example is the usage of aluminium doped zinc oxide (AZO) as a transparent electrode in the replacement of indium tin oxide (ITO). Indium is considered a critical raw material; moreover, an investigation of the life cycle assessment revealed that ITO is more environment burden than AZO [1]. ZnO nanoparticles are used as electron transporting layer in solar cells [2] or light emitting diodes [3]. Another application utilizes the photoluminescent properties of ZnO quantum dots that absorb UV light and re-emit in a visible range, improving power conversion efficiency (down-shift conversion) [4]. Wet chemistry synthesis and solution based deposition methods are currently in demand as they are considered to be low cost and easily scalable techniques for optoelectronic devices production.

The present study discusses the influence of dopant content (Al and Eu) on the structure, morphology, optical, and electrical properties of zinc oxide layers. For the structural characterization Raman spectroscopy was employed, UV-Vis-NIR spectrophotometer and spectrofluorometer were used for optical characterization, thickness and topography were characterized by stylus profilometer and atomic force microscope, and broadband dielectric spectroscopy was used for electrical measurements.

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Preparation of Nanostructured Starch used as Fillers for Bio Hot Melt Adhesives Production

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Hot melt adhesives are widely utilized across various industries, prompting a shift toward the production of bio-based hot melt adhesives to mitigate environmental toxicity [1]. Fillers, integral components of these adhesives, are predominantly used to improve their reinforcing effect [2], and affordability of hot melt adhesives.

Nano starch, a biodegradable, environmentally friendly, and abundant material [3], is synthesized through a process of heating the native starch to induce gelatinization, followed by precipitation in ethanol [4], these substances are modified with chitosan, derived from crustacean shells, to produce biofillers [5].

These nano starch-chitosan fillers were comprehensively analyzed using different instruments and Methods. Dynamic Light Scattering (DLS), Image Analysis (Morphology 3G) were used to determine their morphology, ATR-FTIR was used to identify the different functional groups present in the fillers. The thermal properties were further analyzed using TGA and DSC.

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Strands vs crosslinks: degradation and regelation of poly(butyl acrylate) networks synthesized by RAFT polymerization

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Covalently crosslinked polymer networks, such as thermoset materials are difficult to recycle and reprocess. To overcome this, degradable units can be incorporated into the network structure either within the crosslinker or into the polymer backbone, which can be cleaved chemically to soluble fragments. Which method is more suitable depends on polymerization method, chosen monomer and whether repolymerization of the degraded fragments is targeted.

While degradable crosslinkers containing a disulfide linkage may seem like a simple option, networks made by free radical polymerization (FRP) cannot be reliably degraded using this method. Instead, controlled radical polymerization techniques such as reversible addition–fragmentation chain transfer (RAFT) must be used to afford degradable poly(butyl acrylate) networks at a variety of crosslink densities. In comparison, dibenzo[c,e]oxepane-5-thione (DOT) can be used as a cleavable comonomer with *n*-butyl acrylate, allowing networks made by both FRP and RAFT to be fully degraded. [1]

Both types of degradable networks can produce thiol-functional fragments, suitable for repolymerization by thiol-disulfide exchange. However, structurally these fragments are very different, with fragments formed through disulfide cleavage in the crosslinker having a higher M_n and lower dispersity than the fragments made through the C-S bond cleavage of copolymerized DOT. This difference in M_n and Đ can affect the regelation of these fragments.

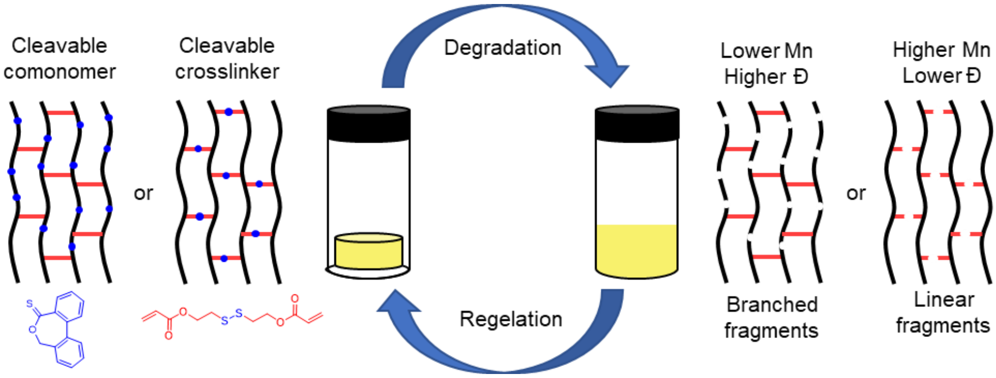

Figure 1: Illustration of degradation of poly(butyl acrylate) networks containing disulfide crosslinker (2,2'-dithiodiethanol diacrylate) or degradable comonomer (dibenzo[c,e]oxepane-5-thione) synthesized by RAFT polymerization.

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The Development of Glycogen-Heparin Hybrids as Biodegradable and In-Blood Active Materials

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Glycogen is a naturally sourced biological nanoparticle that is bio-compatible and biodegradable, which has been leveraged in numerous theranostic applications. Despite its desirable properties, glycogen naturally has minimal in-blood activity, which may lead to rapid immunological responses when the nanoparticles are injected intravenously. Heparin is a bio-active polymer that prevents and treats thrombotic disorders such as deep vein thrombosis, pulmonary embolism, and stroke, through specific interactions with components present in blood. In our work, we look to combine heparin with glycogen as new nanoparticle and hydrogel formulations as low-fouling, biodegradable and in-blood active materials.

The glycogen-heparin combination represents a promising approach for tissue engineering, such as wound healing, inflammation, and thrombosis treatments.

The hybrid materials are designed by thiol-Michael click reactions between thiol-modified glycogen and maleimide-modified heparin. Glycogen was modified with cysteine, endowing the particles with free thiol groups, whilst retaining the native biodegradability. The highly branched roughly spherical form of glycogen keeps during the modification, which was optimised to retain glycogen’s inherent properties. The simple “click” reaction with heparin yielded in-blood active particles (e.g., delays blood clotting in human blood). Separately, we have used similar coupling chemistry to produce hybrid hydrogels by coupling glycogen with multi-maleimide heparin. The gel formation produced high elasticity of 2.0-2.5 kPa with the content of total thiol groups being in the range of 10-15%, and lowering rheological property of 0.8-1.0 kPa in the range of 15-30%. The combination of heparin and glycogen forms a stable and biocompatible gel that can potentially be administered topically. Together, our work demonstrates promising glycogen-heparin hybrid materials for theranostic applications.

Foaming of Polymer Nanocomposites with Chemical Blowing Agents: Effect of Particle Size on Nucleation and Cell Growth

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Polymer nanocomposite foams are cellular materials with sophisticated physical properties such as density, morphology, thermal insulation, and mechanical strength. The typical characteristics of a polymer nanocomposite foam are determined by the nature of the polymer and the size of reinforced nanoparticles. One of the common methods of dispersing gas into a polymer matrix is the addition of chemical blowing agents (CBAs) such as azodicarbonamide (ADC), sodium bicarbonate (SBC), and toluenesulfonyl hydrazide (TSH). ADC ($C_2H_4O_2N_4$) provides controlled expansion during the foaming process. At elevated temperatures (~170-210 °C), ADC decomposes and releases gas such as carbon dioxide (CO_2), carbon monoxide (CO), ammonia (NH_3), and nitrogen (N) that creates bubbles to form inside the polymer matrix. The expansion and density of the foam can be precisely controlled by adjusting the decomposition temperature to get the desired results. To obtain foams with uniform cell size and cell density, the particle size of CBAs is also an important parameter. In this work, polymer nanocomposites of HDPE/SWCNT (99.5/0.5) and HDPE/PTFE/SWCNT (98.5/1/0.5) will be prepared and foamed with ADC by extrusion process. The main objective is to understand the controlled nucleation and growth of cells by reducing the particle size of the ADC since smaller particle sizes have a high surface area which promotes higher nucleation density, resulting in a higher number of smaller and densely packed cells. In a typical extrusion process of polymer nanocomposite foams, pressure, and temperature is the main parameter to be considered for obtaining desired foam morphology with control of the size and uniformity of the ingrown cells. On the other hand, reinforcement of cell walls can be achieved with the help of SWCNT and PTFE inclusions which may also significantly enhances the melt strength and extensional viscosity of the HDPE itself.

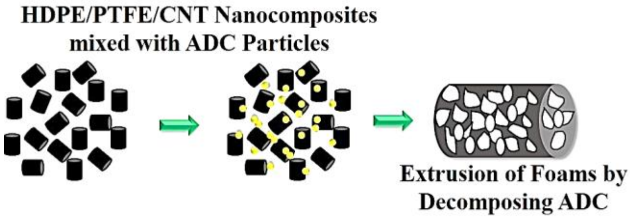

Figure 1: Preparation and Extrusion of Polymer Nanocomposite Foams with ADC

The project was financed from funds of the National Science Centre of Poland based on the decision number NCN OPUS (UMO-2021/41/B/ST8/04036)

P6

Polymer-encapsulated gold nanorods via aqueous RAFT polymerization for biological near-infrared light applications

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Gold nanorods are an attractive nanomaterial for the development of near-infrared light based diagnostic or therapeutic applications such as photoacoustic imaging or photothermal therapy. However, gold nanorods alone lack the required stability and biocompatibility for such tasks [1].

Here, a strategy is presented to encapsulate gold nanorods with a hydrophilic copolymer network using aqueous reversible addition–fragmentation chain transfer (RAFT) polymerization (Figure 1). The composition of the copolymer can be tuned depending on the desired properties of the final material. This not only remedies their drawbacks, but the polymer, if well-designed, could also provide the gold nanorods with additional functionalities. Active-targeting capabilities or drug delivery options would further broaden the use of gold nanorods for near-infrared light based biological applications.

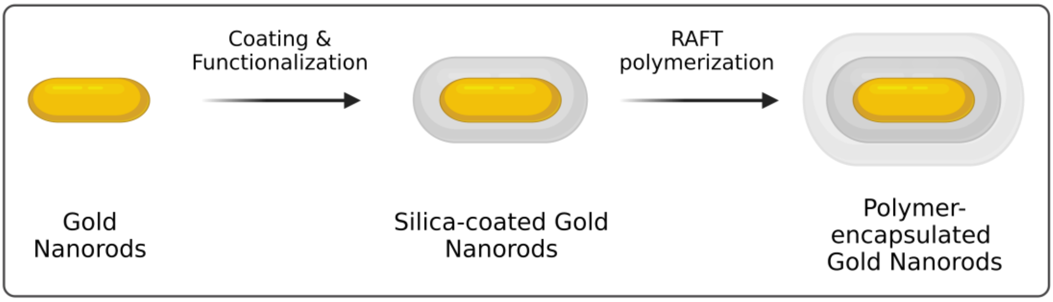

Figure 1: Workflow to obtain polymer-encapsulated gold nanorods. First, the as-synthesized gold nanorods are coated and functionalized, after which RAFT polymerization is performed to generate a hydrophilic polymer network around the particles.

Luise Fanslau gratefully acknowledges financial support by Fonds der chemischen Industrie (FCI).

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Degeneration degree characterization of human cartilage tissues by Raman spectroscopy

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Osteoarthritis (OA), is the main reason of disability of the global population [1]. The disease may be asymptomatic, especially in the early years of its onset. As it progresses, however, pain, stiffness, and a limitation in movement may develop. There are no effective methods to diagnose this disease in its early stages, therefore in most cases a surgical intervention and a prosthetic is necessary.

The scientific project our group is working on, covers the development of the OA diagnostic method with the use of Raman spectroscopy, and also, the design and synthesis of new copolymers with a molecular bottlebrush topology and their applications at various levels of advancement of the degenerative disease. The proposed polymers will serve as a lubricant agent on the damaged joint, decreasing friction and preventing further degradation.

Raman studies are devoted to verification of the possibility to correlate various spectral parameters with changes in chemical structure of cartilage with different degeneration degree [2]. This will help to understand the mechanism of cartilage degeneration and diagnose disease in the early stage. The first stage of our research is an *ex vivo* analysis of the cartilage tissue samples from the patients after total joint replacement. The next stage covers *in vivo* experiments with use of portable Raman spectrometer with an endoscopic fiber optic probe, which can be injected inside the tested joint during the arthroscopy procedure. The *ex vivo* analysis and preliminary results of *in vivo* studies on the animal model will be shown.

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Influence of Heterogeneous Crosslink Density on the Molecular Mobility Modes of Model Epoxy Networks

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Many of the mechanical properties of epoxy networks, such as deformation and fracture behaviors, are largely influenced by the network architecture and microstructure, particularly by their crosslink density and topological heterogeneity [1,2]. The molecular mobility is believed to predominantly influence these macroscopic properties.

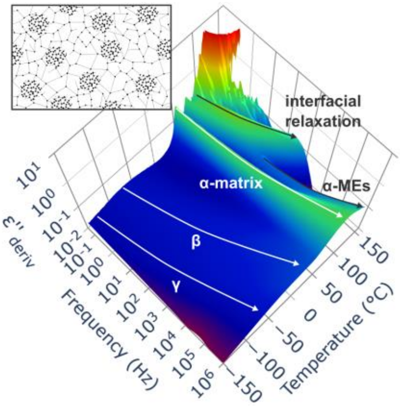

Figure 1: Map of dielectric relaxations in the heterogeneous network.

Series of model epoxy-amine networks with pre-defined heterogeneous architecture were obtained by a two-step protocol. Initially, micrometer-scale reactive crosslinked epoxy microgels (CEMs) were synthesized by precipitation polymerization [3]. Subsequently, these CEMs were introduced into a network of similar chemical nature but having a different crosslink density, in order to achieve topological heterogeneities. Epoxy networks were prepared, from homogeneous (without CEMs) to heterogenous ones displaying zones (former CEMs) having different crosslink densities than the surrounding continuous matrix. The thermal transitions were studied using differential scanning calorimetry (DSC). The low-temperature (γ, β) and glass transition-associated (α) relaxation modes were analyzed by broadband dielectric spectroscopy (BDS) and dynamic mechanical analysis (DMA). The networks that exhibited higher crosslink density contrast between the CEMs and the matrix revealed the presence of two mechanisms related to the glass transitions, T_g, resulting from the two types of networks combined together, i.e. two distinct α-modes.

The BDS measurements also revealed an interfacial relaxation associated with the matrix-CEM interface, which can therefore be considered a signature of the network crosslinking heterogeneity. For each analysis, two consecutive runs were performed, demonstrating the significant influence of absorbed moisture on the molecular mobility modes, particularly the β one.

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Coil-brush polystyrene-*b*-(polyglycidol-*g*-polyglycidol) copolymers. A comparison with linear polystyrene-*b*-polyglycidol

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An original method of synthesis of coil–brush amphiphilic polystyrene-*b*-(polyglycidol-*g*-polyglycidol) (PS-*b*-(PGL-*g*-PGL)) block copolymers was developed for verification of hypothesis that their hydrophilicity and micellization can be controlled by polyglycidol blocks architecture [1,2].

The linear copolymers were composed of polystyrene block with DP_n 29 and of polyglycidol blocks with DP_n 13, 41, 68, 136.

The PS-*b*-PGL with DP_n coil–*b*-brush copolymers were composed of linear diblock with DP_n of polystyrene 29 and 13 of polyglycidol. From the latter the polyglycidol side blocks were grown. The DP_n of these polyglycidol side blocks were 2, 7, and 11.

The copolymers were characterized by ^{1}H-NMR, GPC, and FT-IR methods. The hydrophilicity of films from the linear and coil–brush copolymers was determined by water contact angle measurements in static conditions. Critical micellization concentration (CMC) of copolymers in water was determined by UV-VIS using 1,6-diphenylhexa-1,3,5-trien (DPH) as marker and by DLS. The CMC values for brush copolymers were much higher than for the linear species with similar PGL content. The results of the copolymer film wettability and the copolymer self-assembly studies were related to fraction of hydrophilic polyglycidol in copolymer chains.

This work was supported by the National Science Centre, project entitled "Amphiphilic copolymers containing polystyrene/polyglycidol blocks with varied architecture and their functionalized derivatives—synthesis, properties and aggregation used as carriers of enzymes"
UMO-2018/29/B/ST4/02178

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Impact of various sterilization procedures on polypyrrole coating

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In the work presented here, the effect of sterilisation process conditions on the properties of polypyrrole deposited by electrochemical techniques in the presence of sodium dodecyl sulphate (SDS) was identified. The coatings produced on the surface of SS316 L medical steel were either steam or UV sterilised. By selecting parameters in the electropolymerisation conducted by cyclic voltammetry, films of varying thickness, electrochemical stability and conductivity were obtained. The properties of the films obtained were decisively influenced by the value of the applied potential and the number of scanning cycles.

Investigations of the electrochemical response during doping and de-doping cycles using the CV method showed a stable increase in the flowing charge density during the anode cycle. This was linked to conformational changes occurring in the material immersed in pure electrolyte environment. The application of a steam sterilisation at 120°C for 15 min did not significantly affect the electrochemical stability of the material, nor the conductivity and molecular structure of the polymer films. However, increasing the temperature to 134 °C for a reduced exposure time (3 min) led to degradation of the polymer matrix.

Visible in terms of electrical activity, reduced stability as well as electrical conductivity of the films were recorded. These results were confirmed by the conclusions drawn from the analysis of the recorded FTIR spectra, which were used to determine the conjugation lengths in the chains for fresh materials and materials exposed to sterilisation procedures. A significant effect of ultraviolet radiation was found, which led to a decrease in the adhesion of the polymer layers to the electrode surface, resulting in mechanical damage.

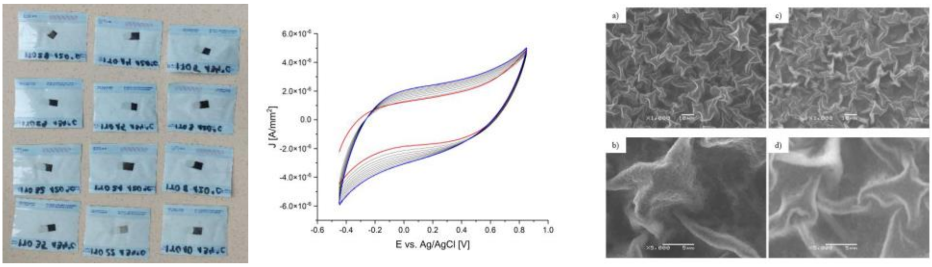

Figure 1: a) Samples sealed for sterilization experiment, b) CV curves of pPy film after steam sterilization (120°C, 15 min), c) SEM images of films after steam sterilization: a), b) 120°C; c), d) 134°C

The work was financed by the Institute own founding.

Impact of ophthalmic drug on the water types trapped in the contact lenses matrix

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Material dehydration is a process of gradual loss of water molecules that is particularly important in hydrogel materials. It is the result of environmental factors to which the material of a contact lens, for example, is exposed. The process begins as soon as the lens is placed on the eye and continues until it reaches a state of equilibrium with the environment. As oxygen is transferred via water molecules in hydrogel materials, excessive loss of water molecules will result in inadequate oxygen supply to the cornea. In the hydrated state of the lens, water molecules interact with the polymer chains, leading to a distinction between the 3 types of water present in the material: highly bonded water (which forms direct hydrogen bonds with polar groups or interacts strongly with ionic residues), loosely bonded water (which forms weaker hydrogen bonds with the lens material) and free water (which does not interact with the base material).

In this study, commercial daily disposable contact lenses based on a silicone hydrogel matrix (Sil-Hy) (material: Omafilcon A) were tested. In a preliminary step, sorption of the ophthalmic drug (dexamethasone) was carried out at selected time intervals (1 or 3 days) and at different initial concentrations of drug (0.05, 0.075 or 0.100 mg/mL), and curves were recorded using differential scanning calorimetry (DSC). Based on the results, the percentages of free and loosely bound water in the test lens material were calculated. The calculations were based on the value of the change in enthalpy of transformation for water.

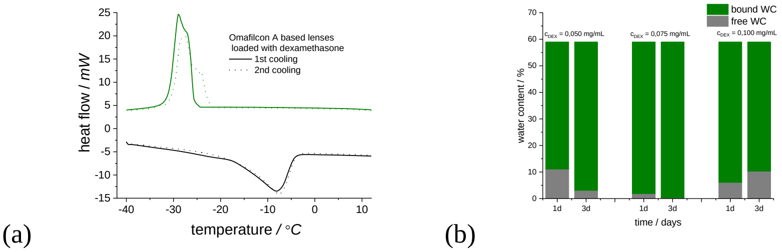

Figure 1: (a) DSC curve for CL loaded with drug (c = 0,05 mg/mL), t = 1 day, (b) water content (%) for free and bonded ones in the Omafilcon A – based lenses

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Influence of stereocomplex formation and matrix phase composition on the thermal and electrical properties of PLA/GNP composites

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Waste from electrical and electronic equipment (WEEE) is one of the fastest growing waste streams in the European Union [1]. What makes it difficult to manage is a large number of different materials in every disposed device, which are difficult or impossible to separate. Recycling of such waste focuses on metals, leaving plastics to landfilling or incineration. Therefore, biodegradable polymers provide an interesting alternative to traditional plastics in electronics. Although their industrial application is still limited due to their insufficient properties, several of them, such as polylactide (PLA), have an interesting capability of stereocomplex (SC) formation, when their two isotactic stereoisomers are mixed. This feature could be possibly used to influence the material's morphology and overcome some of the obstacles [2].

There is strong evidence that the addition of carbon nanofillers, such as nanotubes or graphene oxide, to L-PLA and D-PLA blends has an impact on the SC crystallization kinetics and, consequently, the material's structure [3,4]. However, little research has been done yet on the resulting changes in the composites' thermal and electrical conductivity, which are crucial for applications in electronics. In this work the effects of adding a small amount of graphene nanoplatelets to an equimolar L-PLA and D-PLA blend are studied.

The impact of processing conditions and carbon filler presence on SC formation as well as transition of homocrystallites to SC domains in the composites is studied by differential scanning calorimetry. Raman spectroscopy is used to assess the resulting morphology and filler state. Finally, thermal and electrical properties are investigated to assess the potential of such materials to be applied e.g. in heat management of electronic devices.

The work was supported by the National Centre for Research and Development within the Lider XI Programme (LIDER/11/0031/L-11/NCBR/2020)

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Bottlebrushes - simulation and experimental studies combined

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Polymer bottlebrushes [1] were synthesized by atom transfer radical polymerization (ATRP) with varying degree of polymerization (N_{sc}) of the side chains, poly(methyl methacrylate) (PMMA). Poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (PBiBEM) was used as a macroinitiator with a degree of polymerization $N_{bb} = 102$. Methyl methacrylate (MMA) was used as a solvent after the reaction to equalize all interactions and to maintain good solvent conditions. The concentration of macromolecules in solution was low enough to consider polymer movements only in the vicinity of solvent molecules. As a reference, the linear chains of PMMA in MMA was also investigated in a wide range of chain lengths. The structure and dynamics was studied by light scattering, chromatography, PGSE NMR experiments and by simulations employing of Molecular Dynamics method and Monte Carlo method based on the Dynamic Lattice Liquid algorithm [2]. The experimental values concerning the scaling behavior of polymer size and dynamics were compared and confronted with simulation results.

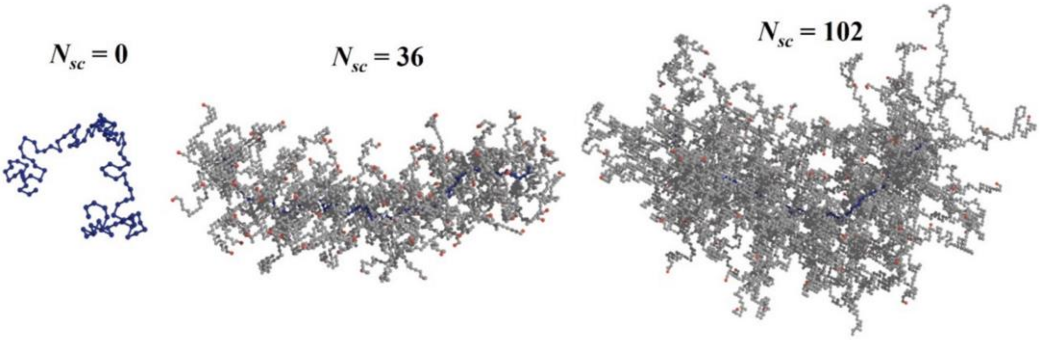

Figure 1: Computer simulation snapshots of PBiBEM-g-PMMA with different side chains lengths. Backbone is presented as blue, red dots represent side chain ends. Solvent is not shown for clarity.

This work was supported by the National Science Centre Poland grant UMO-2017/25/B/ST5/01970

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LIonomers-New Generation of Ionomer: Understanding of their interaction and structuration as a function of the tunability of cation and anion

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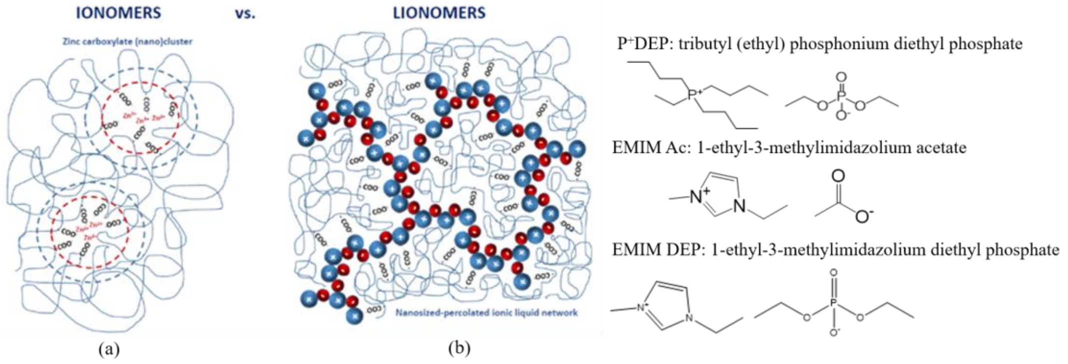
Ionomers are treated as macromolecules possessing one kind of ionic/ionisable groups that are composed of the metal salts (like Zn^{2+}) and acid anions (like carboxylic acids) [1,2]. The microstructure and the properties of such materials depend on both the formation of complex aggregate nodes and their ability to physically cross-link caused by ionic interactions (Figure 1a). On the other side, thanks to the understanding properties of ILs and their limitless anion-cation combinations, the physicochemical interactions can be tuned for designing a new microstructure with relevant functional properties. Herein, three different ionic liquids (ILs) have been considered for designing the new generation of ionomers, *i.e.* LIonomers (Figure 1b), from maleic anhydride grafted polypropylene (PPgMA). The structuration of ILs in LIonomers occurs from a nano/microphase separation process proved by TEM. NMR analyses reveal the existence of ionic–ionic and ionic–dipolar interactions between PPgMA and ILs within LIonomers. Such interactions are highlighted by rheological behavior, and could be also tuned according to the nature of cation (P^+DEP *vs.* EMIM DEP) and anion (EMIM DEP *vs.* EMIM Ac), as well as IL content. Thermal analyses demonstrate that IL could affect the crystallization process according to different pathways. Thanks to the maleic anhydride/IL interactions, an excellent compromise between stiffness and stretchability is obtained paving the way for processing new polyolefin-based materials.



(a) (b)

Figure 1: Schematic of ionomer (a) and proposed LIonomer (b) nano/microstructure

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P15

Synthesis and Characterization of Ultra-High Molecular Weight Hydrogels *via* Photo-initiated Aqueous RAFT Polymerization

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Conventional radical polymerization techniques yield high molecular weight polymers but afford no synthetic control over the polymerization. On the other hand, controlled polymerization techniques afford excellent control but have proved difficult in forming ultra-high molecular weight (UHMW) polymers. Recently, however, synthesis of UHMW linear polymers using photo-initiated controlled radical polymerization techniques has been studied in literature [1].

We set out to synthesize UHMW poly(N,N-dimethylacrylamide) (PDMA) hydrogels and analyze their physical properties. Herein, I describe the formation of UHMW PDMA gels using UV-initiated aqueous reversible addition-fragmentation chain transfer (RAFT) polymerization. The gels were synthesized with targeted degrees of polymerization (DP) between 100 – 100,000 (M_n ~ 990 – 9.9 x 10^6 g/mol) with N,N'-methylenebisacrylamide (MBAm) crosslinker. Equilibrium swelling ratio (ESR), shear storage modulus (*G'*), compression stress and kinetic data were obtained for each targeted DP, while keeping a constant crosslinker loading (10 mol% of MBAm).

Interestingly, both *G'* and ESR tend to plateau at high targeted DP (above 10,000) despite drastically decreased crosslinking density, indicating the formation of highly entangled hydrogels. These entanglements act as transient crosslinks and are responsible for the hydrogel's softness and elasticity, while sparse covalent crosslinks help to maintain its structural integrity [2].

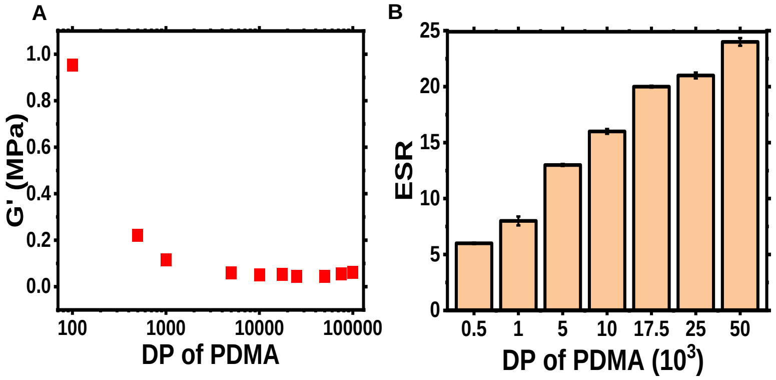

Figure 1: G' at 0.1 rad/s (A) and ESR (H_2O) (B) data for PDMA gels with 10 mol% MBAm.

Acknowledgements: EPSRC New Investigator Award EP/W034778/1.

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Turbidimetry studies of water solution of hydrophobized hyperbranched polyglycidol

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Smart delivery drug systems are of the great interest of scientists now, because they are to solve the problem of poor solubility and low bioavailability of hydrophobic drugs commonly used in therapies. These characteristics leads to necessity of using increased dosages of drugs or prolonged time of therapy, which may cause irritations, pain or even drug resistance. In this case the most desirable drug delivery system should combine hydrophobic and hydrophilic properties to improve hydrophobic drugs solubility in water which is a dominant environment in human body. The usage of hydrogel matrices may be helpful.

Our group suggests using hyperbranched polyglycidol (HbPGL) as a potential drug delivery system. This polymer is obtained in one-pot, relatively easy synthesis [1]; its structure is similar to the structure of dendritic polymers [2] which gives pockets that may be filled with drug molecules. What is also worth mentioning the hyperbranched construction of HbPGL gives an opportunity for further modification [3]. This polymer is also water soluble [4] and biocompatible [1,3,4]. All presented characteristics make HbPGL an interesting material for biomedical applications.

The possibility of modification of monohydroxy groups in the structure of polymer with hydrophobic moieties results in obtaining amphiphilic polymer. The presence of hydrophobic groups in the structure of polymer should prepare an appropriate environment for hydrophobic drug molecules. However, such structural change in polymer influences a thermal behavior of aqueous solutions of polymer, temperature of glass transition or even the rheology of gels prepared from the modified HbPGL [5]. Results of experiments carried out on synthesized polymers will be presented.

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Reversible Capture and Release of (Macro)molecules by Stimuli-Responsive Hydrogels in Microfluidics

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Stimuli-responsive hydrogels have a wide range of potential applications in microfluidics, which has drawn considerable attention. In order to fabricate the next generation of microfluidic devices, we have integrated double cross-linked stimuli-responsive hydrogels [1]. Our device is made of poly(*N*-isopropylacrylamide) (PNiPAAm) and polyacrylamide (PAAm) hydrogel with a permanent cross-linker (*N,N'*-methylenebisacrylamide, BIS) and a reversible cross-linker (*N,N'*-bis(acryloyl)cystamine, BAC). An array of hydrogel dots was integrated into a microfluidic chamber through photopolymerization. The capture and release of the protein bovine serum albumin (BSA) is achieved through thiol-disulfide exchange. Cleavage and re-formation of disulfide bonds of BAC changed the cross-linking density of the hydrogel dots, making them swell and shrink over various cycles. Rheological measurements allowed for selecting hydrogels that withstand long-term shear forces present in microfluidic devices. Reversible capture and release of the protein reached an efficiency up to 84% in release rate and could be repeated over three cycles within the microfluidic device. A similar reversible capture and release of (macro)molecules was reached through host–guest interactions of hydrogel dots with their targets [2]. Adamantane-modified molecules were captured successfully by host–guest interactions formed between the β-CD poly(2-methyl-2-oxazoline) (CD-PMOXA) grafted chains in the hydrogel network and the guest molecules in the solution. Then the captured ones are released by perfusing free β-CD as competing guest molecules. Two kinds of guest molecule, a small molecule and a polymer, were captured and released for three times, with release ratios of 46% and 92%, respectively. The reproducible capture and release of functional molecules with different sizes demonstrated the stability of this microfluidic system and provided an ample platform for flow-through applications in a biomedical context.

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Investigation of new class V-shaped donor-acceptor organic emitters for efficient TADF OLED devices.

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Recently, thermally activated delay fluorescence materials (TADF) have rapidly great attention due to high potential in the field of organic light emitting diode (OLEDs) by utilised the electrically generated triplet excitons and converted into emissive singlet excitons through the reverse intersystem crossing (rISC) to achieve 100% internal quantum efficiency (IQE) [1]. Here, we investigate the effect of variation of the electron-donating ability of a new class of V-shaped donor-acceptor organic emitter based on the donor moiety and the dibenzazepine-based acceptor moiety are separated by a phenylene linker in a V-shaped spatial arrangement and their effect on the photophysical properties. Such spatial separation and electronic decoupling between the donor and the acceptor moieties leads to low singlet-triplet energy gaps (ΔE_{ST}) for high reverse intersystem crossing operations [2]. All investigated compounds showed small (ΔE_{ST}) ranging from -0.23 to 0.12 eV and showed efficient thermally activated delayed fluorescence (TADF) properties. We reported these V-shaped compounds' electrochemistry, photo-physics, and device fabrication characterization. With the structural modification, we can change the luminescence mechanism between the TADF and room-temperature phosphorescence (RTP) and also tune photoluminescence quantum yields (PLQYs) in the range of zero to 30% in various varying polarity of solvents (DCM, THF, Tol), with the solid-state matrices (Zeonex®, CBP) PLQY in the range 2.6 to 36%. Time-resolved spectroscopy analysis in these two matrices revealed the detailed emission properties of these compounds. As for the proof of concept, we constructed solid-state organic light-emitting diode (OLED) devices with (CBP) host, showing a turn-on voltage of around 4.0 V and achieved maximum external quantum efficiency up to 13.6%, based on phenoxazine donor.

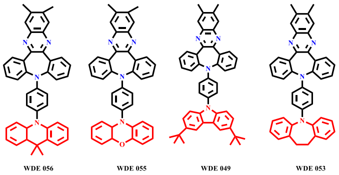

Figure 1: Chemical structure of investigated compounds

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The impact of phenyl insertion on the physicochemical properties of dibenzo[*a,j*]phenazine-based TADF emitters

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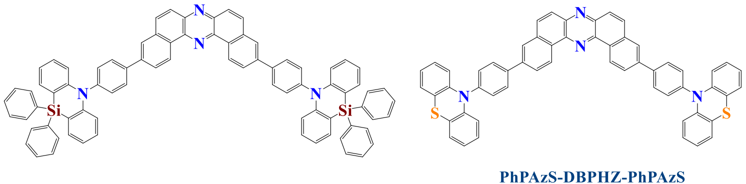
Thermally activated delayed fluorescence (TADF) is a photophysical process in which delayed fluorescence originates from the singlet excited state (S_1) after a short detour from a triplet excited state (T_n) through a process known as reverse intersystem crossing (rISC) [1]. TADF and room-temperature phosphorescence (RTP) have emerged as highly promising emissive materials for efficient organic light-emitting diodes (OLEDs). This is primarily because they possess the ability to harvest electrically generated triplet excitons, making them particularly suitable for OLED applications. The specific utilization of TADF-active purely organic compounds in this research field offers a remarkable advantage by enabling a significantly high external quantum efficiency (EQE) for OLEDs without relying on precious metals like Ir and Pt-based emitters. Therefore, the crucial objectives encompass the development of TADF-active organic compounds, the establishment of materials design through systematic structure-property relationship (SPR) studies and gaining a comprehensive understanding of the TADF mechanism. These endeavours hold paramount importance in advancing OLED technology [2.3]. A novel architecture utilizing a D-π-A-π-D scaffolds exhibiting TADF property has been successfully developed. The design incorporates DBPHZ (dibenzo[a,j]phenazine) as the acceptor molecule [1], along with two distinct donors: Phenyl Phenazothiazine (PhPAzS), Triphenyl dihydrodibenzo azasiline (TPh-DHDBAS). And their photophysical properties were compared with the corresponding D-A-D. Here we would like to present the impact of phenyl insertion between donor and acceptor moiety on the photophysical properties of the emitters.



TPh-DHDBAS -DBPHZ- TPh-DHDBAS

PhPAzS-DBPHZ-PhPAzS

Figure 1: Molecular structures of as-synthesized D-π-A-π-D architecture

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Flexible, printed, organic air-stable resistor

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Resistors are an essential component of most electronic devices. Nowadays, printed electronics is becoming a more and more widely developed field, where the aim is to obtain all electronic components entirely by printing methods. Resistors produced by printing methods must be characterised by high stability of electrical parameters over time, and simplicity of design and manufacture. The inks used to print the resistors must allow the manufacture of resistors with a known resistance at a specific device configuration.

The subject of this work is an organic resistor, fabricated by ink-jet printing, in the structure of which a thin film of poly (3-hexyl thiophene) abbreviated as P3HT is used. The structure of the resistor is shown in Figure 1, where there are comb-shaped electrodes of the device, containing 3 and 5 leads with a fixed distance of 100 micrometres to each other (1), printed by the inkjet method onto a polyester film, covered with a P3HT film of specific geometrical dimensions (2). This polymer undergoes a photo-oxidation reaction in air, in which its molecules undergo permanent chemical changes. After just 70 hours of exposure to a thin film of P3HT, the polymer loses its semiconducting properties, becoming insensitive to an external electric field. P3HT with two average molecular weights of 30 and 100 kDa was used to produce the layers. Layers of 2 x 4 mm and 5 x 5 mm were printed using both types of polymer to produce resistors with 4 different resistances. Then, the printed layer was exposed to light and air for 1 week. After this time, the polymer underwent a complete, irreversible photo-oxidation process that did not progress with time. As a result, resistors with different resistivities from 1.6 MΩ to 42 MΩ were obtained, depending on the surface area of the polymer layer and its molecular weight.

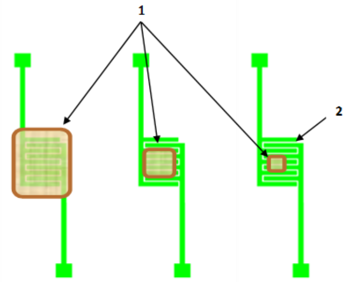

Figure 1: Schematic structure of an organic resistor

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Multi-scale study of the mechanical properties of an epoxy network nanostructured with ionic liquids

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If there are rather a lot of studies in the literature on the deformation mechanisms of polymers in the rubbery or molten state, there are much less on the deformation mechanisms of polymers in the glassy state. Nonetheless, among them, they agree with the fact that the origin of glassy deformations comes from heterogeneities at the scale of a few nanometers (≈ 1 at 10 nm) [1-3]. These heterogeneities often defined as « dynamic » are naturally present in glassy polymer networks, but quite difficult to observe [2]. The goal of the present work is to unveil a better understanding of the influence of nanometric heterogeneities on the large strain behavior and fracture properties of a glassy network.

To study the impact of well-controlled morphologies at the nanometric scale in a glassy network, an ionic liquid (IL) has been introduced in a reference epoxy-amine system. Depending on the chemical nature of the chosen ionic liquid, it can be either fully miscible with the polymer matrix or lead to phase separation [4]. The ionic liquid of this study has been selected as non-reactive to avoid initiating homopolymerisation of the epoxy prepolymer. By establishing relationships between structure, morphology and mechanical properties at different scales, the final goal is to get a better understanding of how the glassy deformation mechanisms propagate through the polymer matrix.

The use of additives in a polymer matrix generally leads to a plastifying effect with a decrease of the modulus and the yield stress, in parallel with an increase of ductility. In our case, the first results in compression and tension after addition of IL show a stiffening effect on the modulus and an increase of the yield stress, while at large deformations, an increase of ductility is observed. To complete the study, DMA and creep tests have also been performed to highlight the impact of IL content on the mobility of the epoxy-amine system both at the molecular and macroscopic scale, and in other words, its ability to deform more or less easily under an applied stress.

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Polarization Free 3D-Printed Piezoelectric Nanogenerators

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In the past few years, portable electronic devices have produced a surge in interest in 3D printable materials and piezoelectric energy harvesters as alternatives to traditional battery systems. The ability to directly print polymer and piezoelectric materials has gained attention for its ability to produce flexible electronic equipment such as sensors, actuators, batteries, supercapacitors, and transistors [1].

Poly (vinylidene fluoride) (PVDF) and its copolymers, such as P(VDF-TrFE) and P(VDF-HFP), are widely used in the production of flexible self-powered energy storage devices due to their outstanding electrical characteristics, flexibility, durability, and chemical resistance. PVDF is a semicrystalline polymer with five crystal phases (α, β, γ, δ, and ε). The β phase, distinguished by its planar zigzag shape, produces materials with solid piezoelectric characteristics [2].

3D printing is a cutting-edge manufacturing process that combines precision computer controls to create polymer-based objects with complicated geometries. However, making piezoelectric devices with PVDF is problematic due to the difficulties of acquiring PVDF material with a high polar phase concentration via fused filament fabrication (FFF) processing. This study describes a novel and effective method for producing piezoelectric PVDF polymer films for energy storage applications. PVDF filament is used in 3D printing. It was discovered experimentally that after 3D printing, a high-based polar phase was acquired, and the open-circuit voltage could be up to ~250 $V_{pk\text{-}pk}$ accomplished in the 3D printing ~0.1 mm PVDF film and could even successfully drive five commercial green LED lights to work normally. The research delves further into the shape, crystallization, and piezoelectric capabilities of 3D-printed PVDF films of various thicknesses.

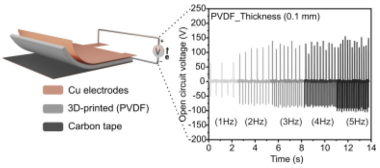

Figure 1: Piezoelectric performance of polarization-free 3D printed PVDF film.

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Radical Ring-opening polymerization of cyclic ketene acetals as a method to obtain branched, biodegradable polyesters

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Microplastics and environmental pollution caused by vinylic polymers are known to be a threat to public health and environment. Following the need for (bio)degradable alternatives, radical ring-opening polymerization (RROP) of cyclic ketene acetals (CKAs) offers a method to synthesize branched polyesters with tunable properties [1,2]. A key feature of RROP is to incorporate various functionalities into the polymer backbone. In the work presented branching was proven to significantly impact macroscopic properties of P(CKAs) like viscosity and melting temperature and could thus be used as a tool to prepare polyesters with tailor made properties. To get an insight how to control the density of branches, kinetic studies on a potential PEG-surrogate revealed, that branching increased with monomer conversion and entirely independent of reaction conditions [3]. In line with earlier studies of a branched PCL, the polymer showed a mixture of two branching types: long chain branching and short chain branching [4]. This polymerization is hence key to develop modern functional polyesters with a wide range of targetable material properties.

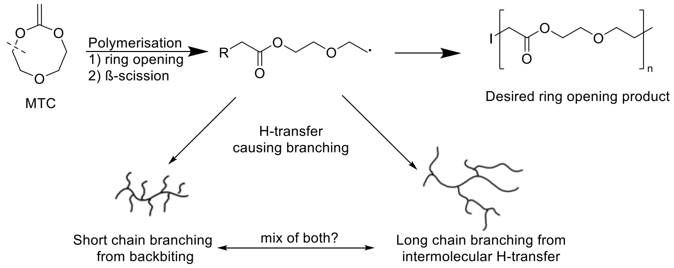

Figure 1: Polymerisation mechanism of the RROP of MTC leading to different branching types caused by H-abstraction within the polymerization.

Acknowledgement: The presented work was supported by a scholarship of the Evonik Foundation.

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Polystyrene core polyglycidol enriched shell microspheres and microspheroids – surface modification with acidic and basic groups

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Primary -OH groups on the surface of polystyrene microparticles with polyglycidol enriched shells P(S/PGL) make possibilities to surface modification by chemical or physical manners. The P(S/PGL) microspheres (with D_n=306 nm) were synthesized by emulsion copolymerization of styrene and polyglycidol macromonomer, using potassium persulfate as an initiator in water. Prolate spheroidal particles were obtained from microspheres by uniaxial elongation of poly(vinyl alcohol) films (PVA) with embedded particles at temperature above T_g of polystyrene and PVA. Finally, the spheroidal particles were isolated by dissolving the PVA film in water. The spheroids were characterized by SEM, DLS, EA, XPS. Negatively charged P(S/PGL) spheroids were obtained by oxidation of native hydroxyl groups deriving from polyglycidol with $KMnO_4$ in the presence of acetic acid. For introduction of basic groups on particles surface the carboxylic groups modified particles were treated with aqueous solution of polyethyleneimine. The modification resulted in positively charged particles over a wide pH range. Positively charged particles were the subject of adsorption studies under various conditions on oppositely charged surfaces.

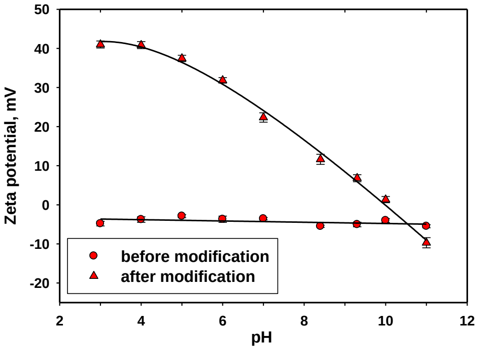

Figure 1: Relation between zeta potential and pH of microspheroids before and after particles surface modification with polyethyleneimine.

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Polypyrrole aerogels as efficient adsorbents for the removal of hexavalent chromium ions from aqueous solutions

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Polypyrrole has attracted much interest among various conducting polymers due to its easy preparation, good chemical and environmental stability, and relatively high conductivity [1,2]. Polypyrrole has been widely used in water treatment for the removal of organic and inorganic contaminants, however, it suffers from low specific surface area and poor mechanical properties [3]. Herein, mechanically stable polypyrrole cryogels were prepared via the oxidative polymerization of pyrrole with iron(III) chloride in the presence of various polymeric stabilizers (poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), gelatin, methylcellulose, hydroxypropylcellulose and nanofibrillated cellulose) under the frozen conditions. The cryogels were later converted into corresponding aerogels through freeze-drying process. The type of stabilizer was found to influence the morphological structure, mechanical and electrical properties of formed polypyrrole aerogels. Scanning electron microscopy images reveal the formation of three-dimensional and highly porous networks with different pore sizes depends on the added stabilizer. All the prepared aerogels were utilized for the adsorptive removal of hexavalent chromium ions (Cr(VI)) from aqueous solutions. The aerogels showed significantly high adsorption capacities of Cr(VI), thanks to their high porosity, specific surface area and ion exchange ability. The maximum adsorption capacity ($Q_{\max}$) of 497.5 mg/g was achieved for the polypyrrole aerogel prepared in the presence of poly(vinyl alcohol) as stabilizer, while the aerogel prepared with poly(*N*-vinylpyrrolidone) showed the lowest $Q_{\max}$ of only 221.2 mg/g.

Acknowledgments: The authors wish to thank the Czech Science Foundation (21-01401S) for the financial support

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In situ resources for the future space colonization: 3D-printed magnetic composites and nanocomposites from Lunar resources.

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Among the several criticalities for future space exploration and colonization is undoubtedly the supply of raw materials for manufacturing every component needed. The utilization of in situ resources present on the surface of a moon/planet, as well as secondary raw materials extracted from end-of-life components, represents the only sustainable solution for long-term Out-of-Earth permanence. Moreover, Additive Manufacturing (commonly known as 3D printing) is a new paradigm of manufacturing with unrivalled freedom of geometry and equipment flexibility, which is ideal for low-volume production and customizability required from the Lunar and Martian exploration. Magnetic materials, both with soft and hard magnetic behaviour, are key components in many devices aboard any spacecraft, such as motors, mechanisms, actuators and sensors. The possibility of manufacturing magnetic components with materials available in situ and through techniques employable in space and on a celestial body is a valuable perspective for the future of space agencies.

The aim of this work is the development of composite and nanocomposite materials with soft magnetic fillers from materials available on the Moon and processable via Fused Filament Fabrication (FFF) 3D printing. Polyether-ether-ketone (PEEK), a high-performance thermoplastic polymer, was chosen as matrix and three different fillers, namely magnetite (Fe_3O_4), nickel-zinc ferrite ($(Ni_xZn_{1-x})Fe_2O_3$) and Fe-Ni alloy, were selected.

Several compositions, from 50 to 80 wt% of filler content, were developed and the polymer matrix rheology was fine-tuned for optimal processing. The raw materials were compounded, extruded into filaments and successfully 3D printed via FFF technique into test samples and technology demonstrators.

All formulations showed thermal and mechanical properties typical of a high-performance polymer composite, with thermal stability up to 600°C, glass transition always above 150°C, high rigidity and retention of mechanical properties at high temperatures, although a reduction in ductility was recorded. The magnetic characterization revealed coercivity, remanence and saturation magnetization values which are very promising for the use in brushless motor components.

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Electro-heating and Conductivity in Silver Metallized Polypyrrole-coated Textile

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Conducting polymers and metal-coated textiles have promising electrical, electrochemical, and biological properties that can be applicable in a broad area of wearable electronics [1,2]. After metallization, conducting polymeric textiles exhibit enhanced electrical properties and might be used in smart wearable electronics.

We report on the silver metallization of the polypyrrole (PPy)-coated textile. Prior to the metallization, the textile was coated with PPy using oxidative polymerization. For metallization, conventional electroplating was modified using different electrolyte media (silver nitrate with acid and/or surfactant) in situ ultrasound bath sonication. The use of surfactant improved the homogeneity of silver deposition on the textile, notably enhancing its conductivity to the level applicable in wearable electronics [1,2]. The metalized textiles without surfactant showed rod-like silver structures and only a small increase in conductivity. Such textile is applicable e.g. as an antibacterial agent [3]. The modified electroplating exhibited flower-like structures. Its sheet resistance decreased from 40 Ohm/sq for PPy-coated textiles to 0.3 Ohm/sq for silver-coated textiles. It has an impact on electro-heating applications: temperature 48°C was reached with Ag-PPy cotton at applied voltage 3.5 V while temperature raised only to 28 °C for PPy coated cotton at 5 V applied.

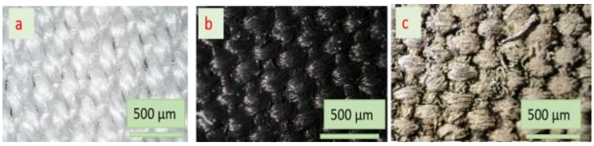

Figure 1: Optical microscopy image of a) cotton, b) PPy-cotton and c) Silver coated PPy-cotton.

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Electronic Memory Effect and Synaptic Plasticity in Thin Films of Diketopyrrolopyrrole-thiophene-based Polymer Doped with Organic Acceptor

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Memristive behavior and the possibility of mimicking synaptic plasticity were investigated in solid-state thin films of conjugated semiconducting copolymer mixed with low-molecular-weight organic acceptor. The polymer, poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2b]thiophene)], DPPDTT was combined with 2-diethylaminopropyl perylene (PDI) in 4 different weight ratios: 1:0, 9:1, 4:1, and 2:1 to explore the impact on memristive behavior.

The devices exhibited bipolar resistive switching showing hysteresis in the current-voltage characteristics. The current ON/OFF ratio up to 10^3, non-volatile memory effect in higher voltage, and synaptic plasticity reminiscent of biological synapses in low-voltage regime with a weight factor of 14% were observed at different operation regimes of the device. These effects were observed when PDI was added to DPP DTT up to 2:1 mass ratio. The electrical switching and hysteresis were attributed to the redox effect of copolymers, the trapping sites created by composites and the formation of space charge at the interfaces between DPP-DTT and perylene domains [1].

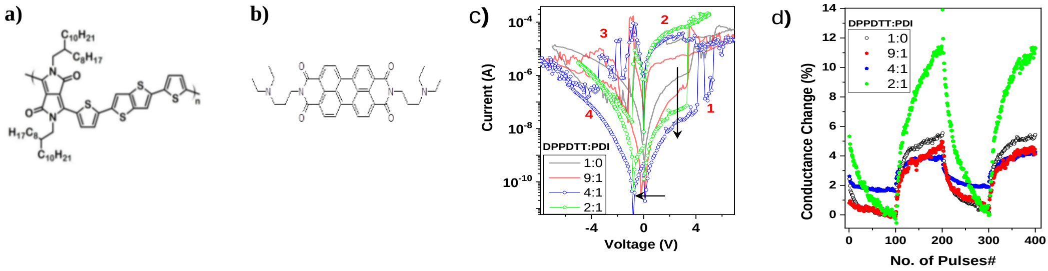

Figure 1: a)-b) chemical structure of DPP-DTT and PDI; c)-d) hysteresis in I-V characteristics and synaptic weight change in composites respectively.

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The influence of crystalline microstructure on interlamellar amorphous phase modulus of polyethylenes

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In our work [1], we presented a universal method for determining the modulus of elasticity of the interlamellar amorphous phase of semicrystalline polymers, based on inducing local deformation of the amorphous phase by using swelling agent (Figure 1). The local strain (ε_a) and local stress (σ_a) of the interlamellar amorphous regions were estimated basing on the changes of the long period (LP) and the yield stress, respectively. The elastic modulus of interlamellar amorphous phase was determined for HDPE (high density polyethylene).

Further research was carried out on relation of elastic modulus of the interlamellar amorphous phase and polymer microstructure. Several methods of solidifying were used on three polymers: HDPE, LDPE (low density polyethylene) and EOC (ethylene – octene copolymer) resulting in different crystallinity degrees. The change of elastic modulus of interlamellar amorphous phase with crystal thickness had linear character. Such relation was justified as a result of decreasing "activity" of α relaxation processes with increasing crystal thickness. [2]

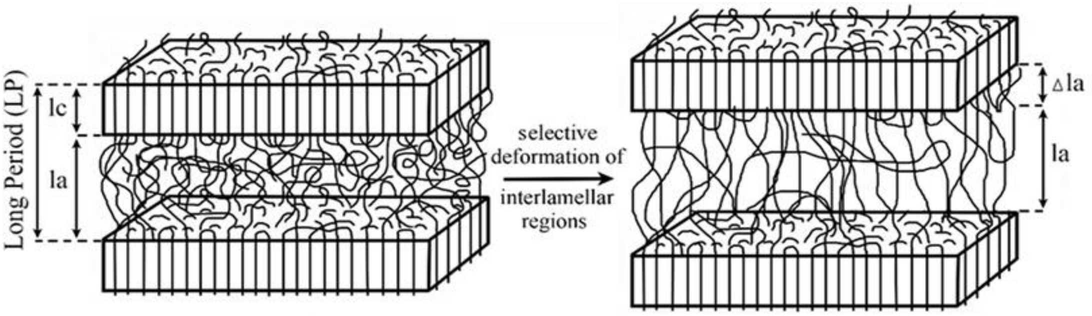

Figure 1: Schematic presentation of selective deformation of interlamellar amorphous regions

Acknowledgments
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Mechanofluorescent Surfaces for Investigating Microscopic Contact Forces at Aqueous Interfaces

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Forces that are “felt” at solid interfaces, termed contact forces, arise from interactions with a pressing medium that can be either another solid or a fluid. These forces are implicated in wide ranging physical and biological phenomena. They determine the adhesion of particles and polymers to surfaces, including biopolymers and tissue[1,2]. A new material basis for investigating contact forces, towards nanoscopic resolution, has been investigated. This approach aimed to challenge traditional approaches of measuring contact forces at aqueous interfaces, by incorporating molecular fluorophores within polymer brush layers as a basis to spatially resolve contact forces in high (nanoscale) resolution. This concept leverages the phenomenon of mechanofluorescence; fluorescence output of polymer brushes that depends on the mechanical conformation of the chains [3-5].

The Surface-Initiated Photoinduced Electron Transfer Reversible Addition-Fragmentation Chain Transfer (SI-PET-RAFT) polymerisation has been used for polymer brushes synthesis with DDMAT-derived CTA RAFT agent. The key polymer backbones consist of poly(N,N-dimethylacrylamide), so as to provide us with a single consistent brush for examining different contact forces. The monomer 2-hydroxyethyl acrylate was used as our functional “handle” to then conjugate fluorophore (Rhod B) by EDC/NHS or isothiocyanate chemistry. The aim of this study understands how to investigate how the retention of the original CTA RAFT end-group influences or hinders polymer brush conformational transitions, and how this can be resolved via studies on mechanofluorescence using Fluorescence Lifetime Imaging (FLIM). Given the clear utility of the SI-PET-RAFT approach for preserving the end-groups, reactive end-groups onto the brushes were exchanged with hydrophilic carboxylic acid groups. Going forward, these surfaces will be used in colloidal AFM studies for elucidating contact forces.

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Polymer bottle-brushes with boronic acid group – dynamic friction studies on Surface Force Apparatus

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The mechanism of function is often altered in the joints due to abnormalities in cartilage structure and loss of synovial fluid. This disease, known as osteoarthrosis, is one of the leading causes of disability in the world population. Abnormalities are manifested by deterioration of tribological properties [1].

The focus of this work is to evaluate the possibility of using bottle brush polymers as joint lubricants. These polymers have a wide range of applications and, due to their structure, have very good lubricating properties, which may be crucial in the treatment of early stages of osteoarthrosis [2].

Surface Force Apparatus (SFA) allows measurement of surface forces between surfaces, such as friction or lubrication [3]. Polymer friction was measured on silver-coated mica surfaces using an SFA 2000 equipped with a digital camera what allowed for the real-time record of the fringes of equal chromatic order. New advanced bottle brush polymers appear to show the ability to reduce the coefficient of friction between surfaces. The tests showed that the diblock structure polymer decreases the coefficient of friction and gives better film stability than the monoblock polymer [4].

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Structural characterization and investigation of shape memory performance of thermoset polyurethane shape memory polymer

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In this study, we present a comprehensive investigation of the structure and shape memory performance of a thermoset polyurethane shape memory polymer PU-SMP with a glass transition temperature of 45 °C, denoted by MP4510. The chemically crosslinked network of this PU-SMP ensures exceptional shape memory behavior, making it highly desirable for various applications. The advantage of this smart polymer is that its activation temperature range is close to room and human body temperature which opens up possibilities for use in biomedical and industrial applications, e.g. fast-response actuators.

In order to better understand the behavior of the material in various conditions and to select the appropriate parameters for the thermomechanical loading program the extensive program of the PU-SMP structural characterization was performed by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The conducted structure characterization confirmed the high strength and high shape memory properties of the PU-SMP.

Shape memory properties, i.e. shape fixity and shape recovery parameters, were determined in the thermomechanical loading program. A modified experimental approach that considered the polymer's sensitivity to external conditions, such as temperature and humidity variations, was applied. The obtained results indicate that the PU-SMP exhibits a shape fixity ratio of approximately 98%, which remains relatively consistent throughout subsequent cycles of thermomechanical loading due to the stability of chemical crosslinks in the thermoset material's structure. In terms of shape recovery, the polymer demonstrated a value of about 90% in the first cycle, which progressively improved to surpass 99% in the third cycle. These findings confirm the positive impact of thermomechanical training on enhancing the shape recovery of the PU-SMP in the subsequent cycles, as well as the influence of thermoset material stability on the repeatability of shape memory parameters.

Acknowledgments: The research has been carried out with the support of the Polish National Center of Science under Grant 2017/27/B/ST8/03074.

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Compostable Household Chemical Bottles Made From Bio-derived and Biodegradable Polymers

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The plastic industry is on the rise and models show that by 2030 we will be producing 460 million tons of plastic waste annually [1]. Due to inappropriate management this waste covers the Earth’s crust and negatively affect natural environment. This drives both scientists and companies to develop more environmentally-friendly packaging materials from such polymers as poly(lactic acid) (PLA), which can be produced from such renewable resources as corn, beet-sugar, or sugar cane [2]. However, some characteristics of PLA (brittleness, reactivity etc.) make it unsuitable for the production of household chemical bottles.

The aim of this research was to design and produce materials that could be utilized in mass-production of compostable, plastic storage bottles for household chemicals. Such bottles would be produced from mainly bio-derived, renewable, and biodegradable polymers. The main materials used for bottle production were PLA Ingeo™ Biopolymer 2003D, hydrolysis stabilizer Stabaxol® P100, chain extender Joncryl ADR 4468, filler Kritilen Filler NC PL830 (60% talc concentrate in PLA), and/or polybutylene adipate terephthalate (PBAT Ecoflex F Blend C1200). Three materials were produced, which were later used to manufacture three-layer bottles by the Extrusion Blow Molding (EBM) method. Materials were characterised by Gel Permeation Chromatography (GPC), ^{1}H NMR, and microscopy, and a number of specific tests was performed on those materials (tensile strength, impact strength, flow rate, hydrolytic stability, and composability tests). The bottles obtained were able to fully decompose in 90 days, they were resistant to media with different pH, and they possessed good mechanical strength.

Research work was carried out as a part of the project “Development of biopolymer composite processing technology (PLA, PHA) and production of multilayer packaging with controllable biodegradation time” No. POIR.01.01.01-00-0781/19 co-financed by the European Union from the European Regional Development Fund under the Smart Growth Operational Program 2014-2021

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Multifunctional Oligocarbonate-based Block Copolymers Acting as PLA's Recycling Aids, Obtained with "a Little Help" from ATRP

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PLA is a very popular material as it is bio-derivable, biodegradable, easily reprocessible, and it has PS-like mechanical properties, so it is durable but brittle [1]. The material is valuable, and it should not be wasted on compost until it is not crucial. However, it is not efficiently mechanically recycled due to polymer degradation (hydrolytic and thermo-oxidative via radicals) occurring at elevated temperatures necessary for polymer processing.

In this work, macromolecular, multifunctional and reactive additives for PLA recycling, were proposed. They could act both as antioxidants and chain extenders. First generation of additives was synthesized by Activator ReGenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) of methacrylates, including glycidyl methacrylate (GMA), utilizing a CO_2-derived elastic core segment as a macroinitiator. During reactive extrusion, epoxide moieties, present in GMA monomeric units of the additives, reacted with -COOH groups present at PLA chains' ends, hence joining together a couple of short PLA chains into big, pom-pom structures. This was proven by the lack of viscosity fall, or even viscosity rise, during reactive extrusion, but also by GPC and AFM results. Generally, the additives were not affecting mechanical properties of PLA but some of them caused slight improvement. The second generation of reactive additives was obtained by opening some of the epoxide rings present in the additives (90, 13, or 5%) with 3,5-di-tert-butyl-4-hydroxybenzoic acid, a chemical with antioxidant properties. The optimum degree of modification (epoxide ring opening) was found to be 5%. Antioxidant properties of chosen additive from the second generation were proven in a UV-degradation test.

Research was funded by POB Technologie Materiałowe of Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme.

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Excellent pH stability and Electroactivity of Electrochemically synthesized DNNSA-doped – Polyaniline (PANI) Films

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Recently, polyaniline (PANI) has been on the front row of conducting polymers as an electroactive material used in designing different bioelectronic devices [1]. It is a unique polymer due to its high electrical conductivity, good environmental stability, good redox activity, and biocompatibility. However, the conducting form of PANI loses its conducting nature at higher pH conditions which limit the applicability and usage of PANI [2]. One way to resolve this issue is to use hydrophobic acids (e.g., PFOS, DBSA or CSA) in preparing PANI to improve and maintain its conductivity at higher pH conditions [3]. In this study, hydrophobic acid, dinonylnaphthalenedisulfonic acid (DNNSA), is used as a dopant in preparing PANI films. Herein, DNNSA-doped – PANI films were prepared electrochemically in a three-electrode cell set-up through cyclic voltammetry. The film produced based on the direct electropolymerization of PANI/DNNSA on glass substrate has been exhibited to conserve its conducting behavior up to pH 8. The UV-Vis spectra of film showed that the conducting form of PANI/DNNSA has been remained for 1 month. The electrochemical stability of the film has improved with 94% retention showing a slow rate of capacitance decrease. Moreover, the electroactivity of films in neutral and slightly alkaline pH were maintained demonstrating an improved electrochemical performance of PANI for higher pH conditions. Therefore, the PANI/DNNSA film prepared with this simple method has showed promising results which can be used for fabrication of bioelectronic devices for tissue engineering, biosensing, and other devices used for regulating various biological and physiological functions in the human body.

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Inkjet Printing of an Electron Injection Layer in organic and Quantum Dots light-emitting diodes

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Inkjet printing is a potential method for manufacturing low-cost and high-resolution organic and quantum dots light-emitting diodes (QLED) for displays/solid-state lighting applications. In this work we are using inverted architecture. We demonstrate commercial aluminium-doped zinc oxide (AZO) film as an electron injection interlayer which was deposited by Super Ink Jet (SIJ) Technology. The SIJ ultra-precision printing onto diverse materials on the sub-micrometer scale, with an internal camera to enable real-time observation. The printer head accurately jets out ink droplets just one-tenth the size and less than one-thousandth the volume of conventional droplets. The printed AZO layer morphology was investigated by means of an optical microscope and an atomic force microscope. The OLEDs based on emissive polymer (Super Yellow) and InP/ZnSe/ZnS Quantum Dots with printed AZO interlayer show a remarkable current efficiency and luminance compared to the OLEDs and QLEDs made without the AZO layer. The possibility of inkjet printing of an efficient electron injecting layer enables in situ patterning of OLEDs' and QLED's emission area. Such a simple and flexible technique can be applied for a wide range of applications such as displays or billboards.

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Synthesis of acid- and amine-containing PPFS derivatives as complementary partners for the construction of multilayer films prepared by layer by layer strategy

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In the fundamental research of nanomaterial field, multicomponent films with tunable properties and structures have received great attention [1,2]. Among the various strategies for constructing films, layer-by-layer (LbL) deposition is a particularly powerful and efficient approach to control the thickness, the internal organization and the surface morphology of the resulting multilayered films, at the nanoscale. Herein, we report on the synthesis of H-bond donor and acceptor partners derived from poly(2,3,4,5-*penta*fluorostyrene) PPFS-based polymers further used as potential complementary building-blocks to prepare LbL films. The *penta*-fluoro-thiol reaction (PFTR) of PFS units was implemented with carboxylic acid [3] and amine-containing thiols, respectively, to synthesize a library of functionalized copolymers that differ in the chemical structure of the modifier (primary *vs* tertiary amine…) and/or the degree of modification of the PFS units. Firstly, mixtures of acid- and base-containing polymers were prepared in solution: as a function of the degree of modification of each partner, structure of the graft, type of solvent, concentration, etc, interpolymer complexes that reveal strong supramolecular interactions between the two PPFS-based partners may be obtained (Figure 1). Then, assembly of films through LbL deposition was undertaken. We present the impact of the previously mentioned variables on some characteristics of the films, such as the growth mechanism (UV-Vis), the thickness (spectral reflectance), the wettability properties (water contact angle) and the morphology (AFM).

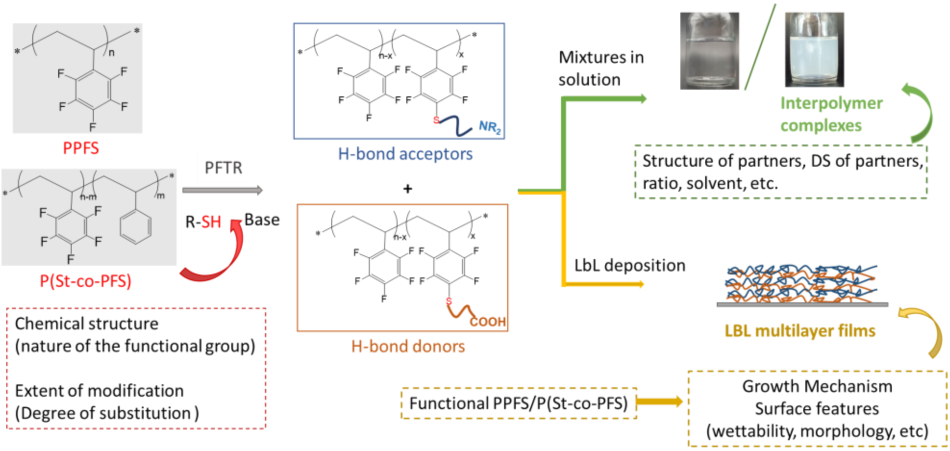

Figure 1: Methodology of the work

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Thermally activated delayed fluorescence in selected exciplexes and the role of local triplet states

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On the way to enhance the efficiency and reliability of the organic light emitting diodes (OLEDs), variety of emitter types have been developed and examined by researchers. Among them, exciplexes in which a succesfull strategy of the efficient harvesting of triplet excitons via thermally activated delay fluorescence (TADF) was implemented gained significant attetnion. It is well-known that in order to realize a forbidden T-S transition between the charge transfer states (CT) the involvement of locally excited ^{3}LE state, localized either on the donor or on the acceptor part as a mediator is needed. TADF process strongly depends on the mutual positions of the locally excited ^{3}LE states and those of the CT character.

In our work, we carefully selected group of five exciplexes with a similar steady state photoluminescence to study the effects of the relative configuration of the ^{1}CT/^{3}CT and ^{3}LE on exciplex TADF. Using a combination of the photo-, electro- and thermo-luminescence studies supported by computational techniques, we demonstrate that upper CT states may serve as substitute mediator states in the absence of obvious ^{3}LE states near the S_1/T_1 manifolds.

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Designing epoxy mixtures towards desired mechanical and electrical properties

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Optimal selection of epoxy materials, curing agents and fillers is a key to obtaining polymer composites with required physical properties [1,2]. The presented work compares properties of several cured epoxy resins, obtained from different epoxy monomers and curing agents with addition of various fillers. Differential scanning calorimetry (DSC), broadband dielectric spectroscopy (BDS) and optical observations were used to determine the properties of the monomers and the cured products. First, we used an epoxy monomer based on bisphenol A, cured with a typical diamine and an acid. In that case, the choice of an acid as a curing agent had significant impact on decreasing the glass transition temperature, as well as on the visibility of a relaxation process in the obtained products. Next, we investigated a nematic epoxy monomer with long aliphatic chains, a triaromatic mesogen and nonterminal epoxy groups. Products of curing this monomer with the same amine have notably lower glass transition temperatures and higher elasticity, as compared to the first monomer based on bisphenol A. We then attempted to stabilize the structure of these products by using fillers: silicon dioxide and titanium dioxide. Introduction of fillers led to vanishing of relaxation processes at low temperatures and increasing the glass transition temperature. Different mechanisms through which the fillers get embedded into the matrix structure were reflected in the obtained results.

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Studies on the Synthesis and Characterization of Sustainable Hydrophobically Modified Ethoxylated Urethanes

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Conventional hydrophobically modified ethoxylated urethanes (HEURs) are telechelic polymers containing a water-soluble core end-capped with hydrophobic groups, which increase the viscosity of aqueous solutions by forming micelle-based networks. Despite the broad applicability in paints, inks, or coating products, the sustainability of this class of materials remains an open issue because of the safety concerns regarding the application of toxic diisocyanates during their synthesis.

In response to these issues, we obtained a new class of isocyanate-free hydrophobically modified ethoxylated poly(hydroxy-urethane)s (IFHEURs). The first step involved the preparation of CO_2-based hydrophilic IFHEUR prepolymer through aminolysis of five-membered poly(ethylene glycol) bis(cyclic carbonate) using a molar deficiency of 4,7,10-trioxa-1,13-tridecanediamine. It was further extended in a reactive extrusion (REX) synthesis using bio-based hydrophobic fatty diamine. The REX technique made it possible to overcome the typical limitations of the aminolysis reaction and to reach the desired conversion within a moderate reaction time.

Importantly, their synthesis route not only omited isocyanates, but also used CO_2 as a building block incorporated during the formation of the bis(cyclic carbonate) monomer. Thus, the resulting architecture of PHUs imparted unique properties, not present in the standard PU materials.

IFHEURs have been structurally elucidated using FT-IR and NMR spectroscopy techniques, MALDI-ToF mass spectrometry, SEC analysis, as well as rheological measurements. The studies of their associative behavior in aqueous solutions confirmed that the architectural flexibility of the obtained IFHEURs, containing terminal and pendant hydrophobic groups, as well as pendant hydroxyl groups, opened a perspective for tuneable thickening performance [1].

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Molecular dynamics and structure of amino functionalized PMMA copolymers

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Modern electronic devices require dielectric materials with precisely controlled properties, such as those needed for gate dielectrics, embedded capacitors, or electrostrictive actuators. Over the last years, there has been an exponential increase in interest of flexible electronics, especially organic thin-film transistors (OTFTs). An application of dielectric layer possessing elevated value of dielectric permittivity between the gate electrode and the organic semiconductor layer is of crucial importance for desired operation parameters of organic thin films transistors, since it allows reducing power consumption of the devices by using lower drive voltages.

The main purpose of this work is to characterize new synthetized solid-state dielectric materials and their molecular dynamic and structure. The materials investigated are amino functionalized PMMA-based samples that were obtained by free radical copolymerization of methyl methacrylate (MMA) and 2-aminoethyl methacrylate hydrochloride (AMA), employing AIBN as radical initiator. A series of statistical copolymers with various MMA : AMA ratios were obtained, i.e., 95:5; 90:10; 85:15. For their investigations Broadband Dielectric Spectroscopy (BDS) and Differential Scanning Calorimetry (DSC) have been employed.

The conducted research revealed that the obtained copolymers have an amorphous structure and exhibit elevated electrical permittivity, as compared to neat PMMA. This results from the presence of amino groups introduced into their structure. The applied modification affects the segmental and local dynamics of PMMA, changing the network of intermolecular interactions in the studied copolymers.

The obtained copolymers meet the requirements for dielectrics to OTFTs and will be further tested in such systems.

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Porphyrin derivatives as multifunctional materials – analysis of electrochemical and spectroelectrochemical properties

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In recent years, there has been a significant increase in interest in multifunctional electro- and photoactive organic materials with properties that allow them to be used in organic electronics, optoelectronics and photovoltaics. They have the ability to quickly and reversibly react to an external stimulus (electrical voltage and light), high electrochemical stability and absorb electromagnetic radiation in a wide range of wavelength. Electroactive materials are used for example in organic light-emitting diodes (OLEDs), displays and sensors [1]. On the other hand, photoactive compounds such as porphyrins are popular materials in photodynamic therapy (PDT). They may contain a cation of metals, located centrally in the ring, and can be substituted with groups of various chemical character [2], e.g. conductive units, which allows to obtain both photoactive and electroactive material. In these studies, the influence of the presence of a zinc cation in the porphyrin ring and the type of organic substituent: α-terthienyl and 3,4-ethylene-1,4-dioxythiophene on the electrochemical and spectroelectrochemical properties was examined. The electrochemical analysis was carried out by cyclic voltammetry and the characterization of the spectroelectrochemical properties was performed by UV-Vis-NIR spectroelectrochemistry. These measurements made it possible to assess the electrochemical stability and the reversibility of the redox processes, as well as to determine the effect of the applied potential on the optical properties of the tested compounds.

The presence of groups with conductive properties and the porphyrin ring is of key importance from the point of view of multifunctionality and creates a chance to obtain new materials with desirable properties in electrochromic devices and organic solar cells.

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Carbon dioxide adsorbing polyhydroxyurethanes with amine groups and their thermal cycling degradation

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Currently used technologies of carbon dioxide capture are based upon hydroxides, ion-exchange resins or immobilised amines adsorption. Approach of active amine entrapment in polyhydroxyurethane molecules was proposed in our previous work [1-2].

Stability and thermal cycling resistance are now most common researched parameters for amine or amine functionalised sorbents in CO_2 capture. In this work, amines immobilised within polyhydroxyurethanes structure were synthesized from five-membered cyclic carbonates based on Bisphenol A diglycidyl ether, diglycidyl ether and trimethylolpropane triglycidyl ether, then coated onto silica fume. Resultant particles were tested for adsorption capabilities and thermal cycling in ambient air of ~420 ppm CO_2 and 40% relative humidity. In time, sorbents showed no adsorption capability deterioration and thermal cycling degradation was simulated by 90°C/40% humidity/atmospheric air incubation. Polyhydroxyurethanes syntheses and thermal degradation mechanisms were explored by FTIR, ^{1}H and ^{13}C NMR spectroscopy. Obtained polyhydroxyurethane-coated silica fume adsorbents were able to adsorb up to 72.6 $mgCO_2/g_{ads}$ and be stable for minimum of 5 regeneration cycles with no change in adsorption capability.

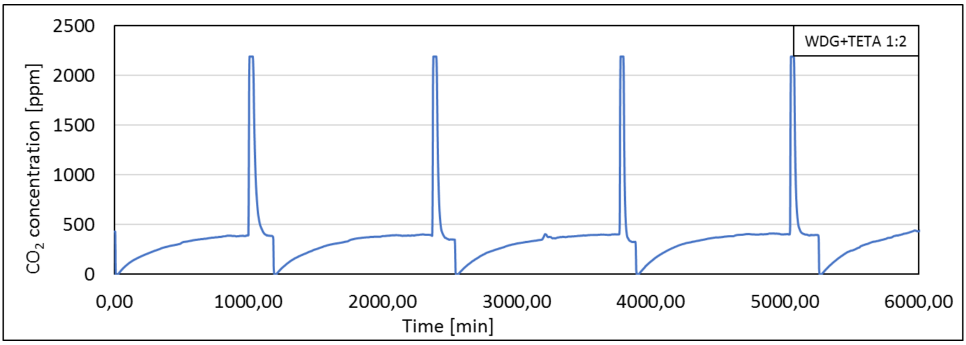

Figure 1: Carbon dioxide concentration on the outlet of the adsorbent bed (WDG+TETA 1:2) during adsorption and thermal assisted desorption cycling.

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