7TH YOUNG POLYMER SCIENTISTS CONFERENCE AND SHORT COURSE

PROGRAM AND ABSTRACTS

Lodz University of Technology

Faculty of Chemistry

Department of Molecular Physics

27-28 September 2021, Lodz, Poland, online

PREFACE

The European Center for Nanostructured Polymers (ECNP Scarl) is a non-profit limited liability consortium formed by the European Network of Excellence "Nanofun-Poly"(FP6 EC). Lodz University of Technology is one of the founders and shareholders of ECNP.

The tradition of the ECNP conference dates back to 2004. In order to maintain contacts and exchange knowledge, it was decided to organize on-line the 7th Conference and Short Course for Young Polymer Scientists. We are convinced that thanks to the participation of excellent lecturers from leading European research centers, the set goals will be achieved.

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7thYoung Polymer Scientists Conference & Short Course, 27-28. 09. 2021, Lodz, Poland

Scientificprogram of tutorial lectures (**T**) and young scientists'short communications (**Y**)

Monday, September 27th, webinarium		
8:40 – 9:00		Opening Ceremony
Chairperson: Jacek Ulański	9:00 – 9:40	(T1)**Andrzej Gałęski**, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland ***Processing induced strengthening of polymers***
	9:40 – 10:20	(T2)**Krzysztof Matyjaszewski**, Carnegie Mellon University, Center for Macromolecular Engineering, Pittsburgh, USA, & Lodz University of Technology, Department of Molecular Physics, Lodz, Poland ***Nanostructured Polymers and Nanocomposites by ATRP***
	10:20 – 10:35	**(Y1) Helen Pfukwa**, Department of Chemistry and Polymer Science, Stellenbosch University, Stellenbosch, South Africa ***Bio-based aldehyde-functionalised polymers by reverse iodine transfer polymerization***
	10:35 – 10:50	**(Y2)Mahrukh Sadaf**,Department of Enterprise Engineering "Mario Lucertini", and INSTM RU Roma-Tor Vergata,University of Rome "Tor Vergata", Rome, Italy ***Properties and processing of multi-component thermoplastic binder systems for extrusion-based additive manufacturing***
10:50 – 11:30		COFFEE BREAK
Aleksandra Wypych-Puszkarz	11:30 – 12:10	(T3)**Andrzej Rybak**,ABB Corporate Technology Center, Krakow, Poland ***Influence of polymer processing on thermal conductivity of nanocomposites***
	12:10 – 12:50	(T4)**Francesca Nanni**, University of Rome Tor Vergata, Italy ***Present trend of polymers and composites application in the aerospace sector***
	12:50 – 13:05	**(Y3)Piotr Węglarski**, Department of Molecular Physics, Lodz University of Technology, Lodz, and Corning Optical Communications Sp. z o.o., Strykow, Poland ***Stripping the primary coating layer from the fiber optic surface***
13:05 – 14:15		LUNCH BREAK
Lidia Okrasa	14:15 – 14:55	(T5)**Rebeca Hernandez**, Institute of Polymer Science and Technology (ICTP-CSIC), Madrid, Spain ***Polymer hydrogels and their composites with nanostructured particles: from preparation to advanced applications***
	14:55 – 15:35	(T6)**Beata Łuszczyńska**, Department of Molecular Physics, Lodz University of Technology, Poland ***Organic photodetectors for NIR biological tissue window***
	15:35 – 15:50	**(Y4)Ulrike Staudinger**, Leibniz-InstitutfürPolymerforschung, Dresden, Germany ***Dispersion and electrical percolation of shortened carbon nanotubes in styrene-butadiene based block copolymers***
	15:50 – 16:05	**(Y5)Busra Findik**, Ingénierie des MatériauxPolymères, Université Claude Bernard Lyon, Lyon, France ***Synthesis of new nanocomposites based on magnesium and silicon by the combination of in situ sol-gel chemistry and reactive extrusion***
	16:05 – 16:20	**(Y6)Jakub Szewczyk**, NanoBioMedical Centre, Adam Mickiewicz University, Poznan, Poland ***A novel, ultrathin 2D-like polydopamine membranes from the air/water interphase – tuning polymerization process towards better understanding of their nanostructure***
16:20 – 16:40		COFFEE BREAK
16:40 – 18:40		**Poster session I**
19:00 – 21:00		**Poster session II**

Tuesday, September 28th, webinarium		
Marcin Kozanecki	8:30 – 9:10	(T7)**Brigitte Voit**, Leibniz-InstitutfürPolymerforschung, Dresden, Germany ***Synthesis of functional polymeric materials for optoelectronic applications***
	9:10 – 9:50	(T8)**Jiri Pfleger**,Institute of Macromolecular Chemistry, Czech Academy of Sciences,Prague, Czech Republic ***Application of polymers in solution processable organic electronic devices.***
	9:50 – 10:05	**(Y7)Angelika Wrzesińska**, Department of Molecular Physics, Lodz University of Technology, Lodz, Poland ***Investigation of molecular dynamics of poly(dimethylsiloxane) cross-linked by metal-ligand complexes by broadband dielectric spectroscopy***
	10:05 – 10:20	**(Y8)Mario Iván Peñas**, Institute of Polymer Science and Technology (ICTP-CSIC), Madrid, and University of the Basque Country, Donostia-San Sebastián, Spain ***Nanostructured thin films obtained by dip-coating poly(butylene succinate), poly(ε-caprolactone) and their copolyesters (PBS-ran-PCL)***
10:20 – 11:00		COFFEE BREAK
Beata Łuszczyńska	11:00 – 11:40	(T9)**Paul Blom**, Max Planck Institute for Polymer Research, Mainz, Germany ***Charge transport in organic semiconductors***
	11:40 – 12:20	(T10)**Yingping Zou**, Central South University, Changsha, China ***Organic polymer optoelectronic materials***
	12:20 – 12:35	**(Y9)Krzysztof Jerczyński**,Institute of Polymer and Dye Technology, Lodz University of Technology, Lodz, Poland ***Molecular brushes used as templates for titanium dioxide nanoparticles synthesis***
	12:35 – 12:50	**(Y10)Andrzej Świeży**, Faculty of Chemical Engineering and Technology, Cracow University of Technology and Photo HiTech Ltd, Cracow, Poland ***One-component cationic photoinitiators for preparation semiconductor nanoparticles filled photopolymer composites***
12:50 – 13:50		LUNCH BREAK
Gabriela Wiosna-Sałyga	13:50 – 14:30	(T11)**Stefan Jurga**, NanoBioMedical Centre, Adam Mickiewicz University, Poznan, Poland ***Nanomaterials for biomedicine***
	14:30 – 15:10	(T12)**Tsuneo Hagiwara**, Yokohama National University, Yokohama, Japan ***Photocurable resin for 3D Printing***
	15:10 – 15:25	**(Y11)Sonal Gupta**,Institute of Macromolecular Chemistry, Czech Academy of Sciences,Prague, Czech Republic ***Enhanced antibacterial activity of polypyrrole with tunable conductivity, morphology and capacitance by acriflavine hydrochloride***
	15:25 – 15:40	**(Y12)Tatiana Statsenko**, ITMO University and N.E. Bauman Moscow State Technical University, Moscow, Russia Federation ***Optically active nanocolloidal ink for 3D printing***
15:40 – 16:00		COFFEE BREAK
Piotr Polanowski	16:00 – 16:40	(T13)**Jean-Francois Gérard**, National Institute of Applied Sciences of Lyon-INSA, France ***Building of polymer networks: focus on gelation phenomenon***
	16:40 – 17:20	(T14)**Krzysztof Hałagan**, Department of Molecular Physics, Lodz University of Technology, Lodz, Poland ***Computer simulations of non-equilibrium phenomena and complex polymer systems with cooperative dynamics***
	17:20 – 17:35	**(Y13)Ron Dockhorn**, Institute Theory of Polymers, Leibniz Institute of Polymer Research, Dresden, Germany ***Polymer architectures by chain walking catalysis - theory, simulations, and experiments***
17:35 – 18:00		Concluding remarks
18:00 – 20:00		**Poster session III**

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LECTURES

MONDAY, SEPTEMBER 27TH, WEBINARIUM

Processing induced strengthening of polymers

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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 most efficient controlled/living 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. 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 and nanocomposites were prepared with high precision.

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[2] Malakooti, M. H.; Bockstaller, M. R.; Matyjaszewski, K.; Majidi, C., Liquid metal nanocomposites, *Nanoscale Advances***2020**, *2*, 2668-2677.

[3] Yan, J.; Bockstaller, M. R.; Matyjaszewski, K., Brush-modified materials: Control of molecular architecture, assembly behavior, properties and applications, *Prog. Polym. Sci.***2020**, *100*, 101180.

Bio-based aldehyde-functionalised polymers by reverse iodine transfer polymerisation

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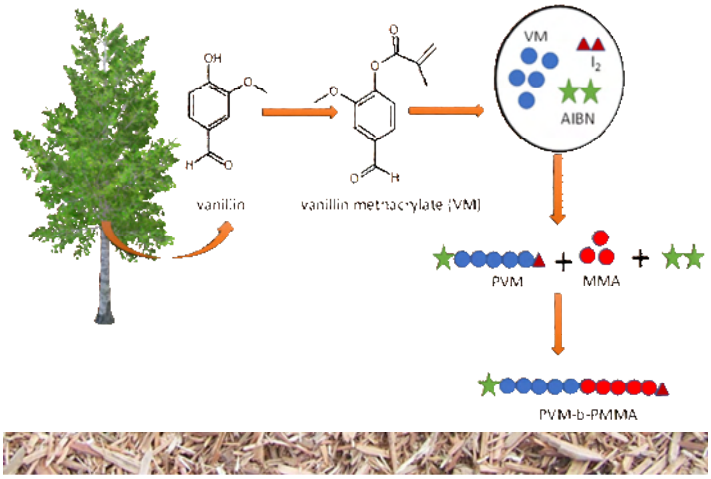
Bio-based polymers with reactive functionalities are becoming increasingly attractive as they address some critical global concerns related to sustainability. In this work vanillin methacrylate (VM), an aldehyde functionalised monomer synthesised by the methacrylation of vanillin (a lignin-derived compound) was polymerised via reverse iodine transfer polymerisation (RITP) [1, 2]. The influence of various reaction parameters including the polymerisation solvent, the initiator-to-iodine ratio and the polymerisation temperature on the induction (inhibition) period and polymer molar mass was investigated by ^{1}H NMR spectroscopy and size exclusion chromatography. The lack of a clear and consistent discolouration of the reaction mixture to indicate the end of the induction period in the solvents investigated, i.e. toluene, methyl ethyl ketone (MEK) and *N*,*N*-dimethylformamide (DMF), was an indication that iodine was taking part in a side (complexation) reaction with the solvent. When the monomer conversions were followed by ^{1}H NMR spectroscopy it was found that the induction periods for the reactions carried out in MEK and DMF were significantly shorter due to the consumption of iodine by VM, leading to the formation of a new chain transfer agent (CTA) 4-formyl-2-methoxyphenyl 2-iodo-2-methylpropanoate [3]. The formation of polymer chains derived from this CTA was confirmed by matrix assisted laser desorption/ionisation time-of-flight-mass spectrometry. Todemonstratethe "livingness" ofthe polymerisation process, PVM was chain extended with methyl methacrylate. The formation of block copolymers was confirmed by high performance liquid chromatography. The application toolbox of these polymers was expanded by the formation of various poly(vanillin methacrylate) Schiff base polymers endowed with additional functional groups.



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[3] T. Wright, H. Chirowodza, H. Pasch, *Macromolecules* **2012**, *45*, 2995–3003.

Properties and processing of multi-component thermoplastic binder systems for extrusion-based additive manufacturing

Mahrukh Sadaf[1], Santiago Cano[2], Joamin Gonzalez.Gutierrez[3],M. Bragaglia[1], Stephan Schuschnigg[2], Christian Kukla[4], Clemens Holzer[2], F. Nanni[1]

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Additive manufacturing (AM), also termed 3D printing, is defined as the process of joining materials to create objects from 3D model data, usually layer by layer, commanded by the digital model as opposed to subtractive manufacturing methodologie [1]. AM has induced huge attention nowadays. It is rapidly moving from research to commercial applications because of its capability to manufacture complex geometric features, which are difficult or less feasible to develop by traditional machining. The most applicable Additive Manufacturing technologies majorly use powder, pallets, or filament as the primary source that are selectively melted through a focused heat source and proceeded by solidification through successive cooling to manufacture a component [2].

The low-cost material extrusion (MEX) additive manufacturing technology can offer an economical alternative to manufacture metal parts with complex geometry over traditional manufacturing. This work aims to better understand the type of thermoplastic compounds required to produce filaments of highly loaded metallic fillers that can be successfully printed via MEX[3]. Compounding of feedstock material with metals and binder systems was done. The rheology and processability of the feedstocks were studied. Based on the preliminary trials, the printing temperature and other parameters were selected for shaping the MEX parts. It was observed that the filaments could be printed with acceptable quality.Further, debinding was performed to remove the binders from the 3D printed specimens. The final step was sintering, where the specimens were heated at an elevated temperature under a reductive atmosphere, and the resulting metallic parts have been characterized. The results show that sintered metals have90-94% of the theoretical density and the characterization confirms that the post-processing under reductive atmosphere protected the samples from oxidation.

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Thermally conductive polymer composites – influence of fillers and processing

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Polymer composites are commonly used in the electronic and power devices as an electrical insulation. The management of heat dissipation is crucial for ensuring the proper operation of electrical devices. Improper heat management can potentially lead to malfunctions. Optimized thermal management in electronic components can lead to a reduced carbon footprint or to an enhanced rating of their power ranges. The addition of particles into a polymer matrix can result in a significant improvement of its thermal conductivity [1].

The appropriate selection of the filler and the processing methods used for preparation of the polymer composite is a key step to control and obtain the optimized and desired properties. Distinctively, the quality of the filler–matrix interface seems to be crucial in ensuring the conductive properties of a composite. In particular, it is necessary to consider the phonon scattering processes as well as the interface resistance. To increase thermal conductivity in polymer composites, the conductive paths must be maximized, and the thermal contact resistances must be reduced. Thus, one should select the most suitable filler and processing method that will lead to a polymer composite with appropriate thermal conductive functionality.

For this reason, the modification of the filler materials can give a promising solution. A several methods for the thermal conductivity enhancement will be discussed, namely:

- incorporation of the hybrid nanofillers (e.g. graphene nanoplatelets) [2], and the microfillers (e.g. boron nitride flakes) [3],
- use of the magnetic field-assisted filler alignment technology [4],
- synthesis and application of a novel core-shell materials [5][6].

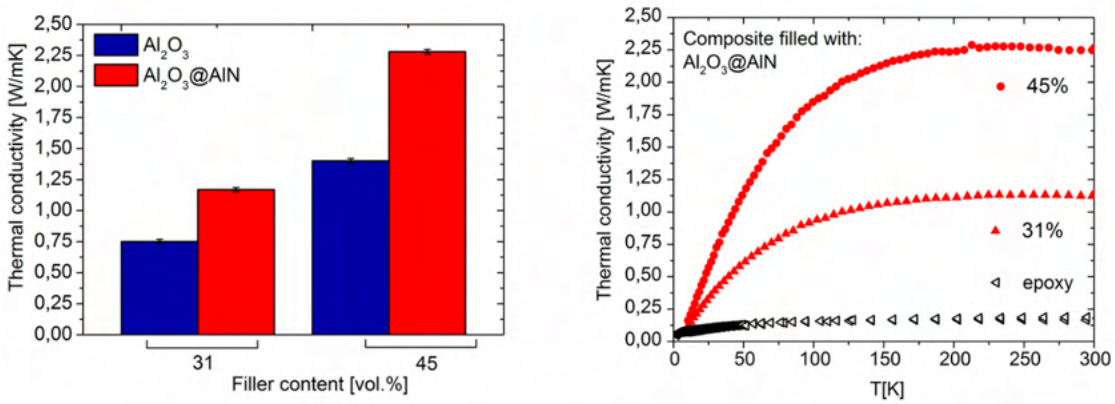

Figure 1: Thermal conductivity of composites measured at 300K with core-shell fillers in relation to standard system (left). Temperature dependence of thermal conductivity measured for composites filled with Al2O3@AlN core-shell particles with different filler content (31 and 45 vol.%). For comparison the dependence for neat epoxy is shown [5].

The composite samples based on epoxy resin filled with the modified fillers have been investigated in order to determine the effective thermal conductivity. The obtained composite samples exhibited a significant improvement in the thermal conductivity (see examples in Figure 1 and Figure 2). The results were analyzed with use of the various theoretical models. Additionally the mechanical and the dielectric measurements were performed showing a high potential for the composites with incorporated new modified fillers to be applied for the electrical insulation with the enhanced thermal conductivity [7].

The evaluation of a possible application of the functional shrinkable materials in the thermally conductive electrical insulation elements was investigated [8]. The effectiveness of gamma radiation on the crosslinking of a selected high density polyethylene grade was analyzed. The crosslinked polymer composites filled with boron nitrideshowed the enhanced thermal conductivity. The shape memory effect was fully observed on the crosslinked samples with a recovery factor reaching nearly 99%. There was no significant influence of the crosslinking, stretching and recovery of the polymer composite during shape memory

phenomenon on the value of thermal conductivity (see Figure 3). The proposed boron nitride filled polyethylene composite subjected to crosslinking is a promising candidate for fabrication of the thermally shrinkable material with the enhanced heat dissipation functionality for the application as electrically insulating components.

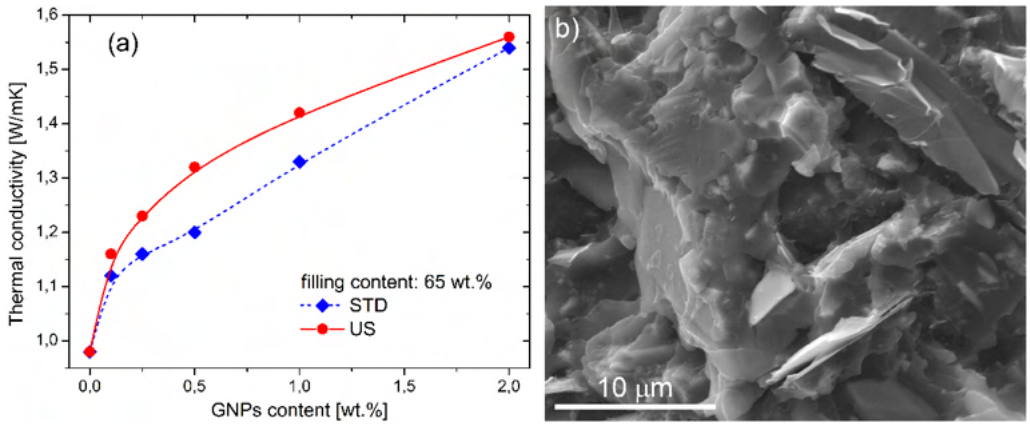

Figure 2:(a) Influence of the preparation method on thermal conductivity of nanocomposites filled with a mixture of microsilica and graphene nanoplatelets (STD – standard method, US – method with ultrasonication step), (b) SEM image of sample fractures with visible graphene nanoplatelets between microsilica grains [2].

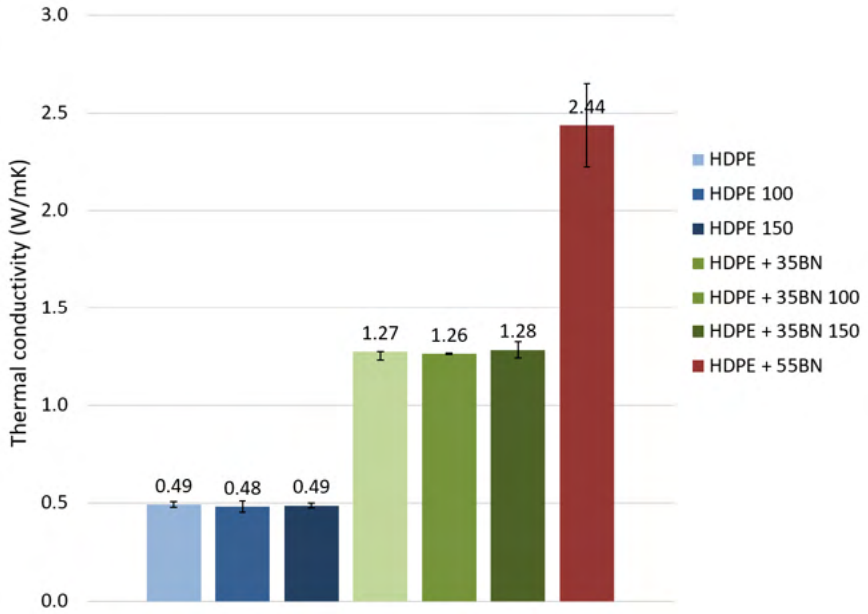

Figure 3: Thermal conductivity measured perpendicularly to injection molding direction for samples with different content of BN. Results for reference pristine samples and samples after testing shape memory effect.

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Present trend of polymers and composites application in the aerospace sector

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In recent years, the Aerospace sector has experienced many changes, which involve the economy, the services offered, the products, processes and materials [1]. The new scenario foresee the launch of constellations of micro/nano satellites, launchers able to sustain more than one mission, colonization of the space, deviation of celestial bodies, to cite a few. In the background, the target of sustainability and clean space is clear and needs to be pursued. The material innovation is in the hearth of many space developments, where increased performance, multifunctionality, decrease of the weight, higher resistance to harsh environment (included radiations) and temperatures, recyclability/sustainability are the most required targets. In many cases, reinforced polymers and composites are key materials. In particular, engineering thermoplastics (as PEEK, PEI, etc.) can offer good mechanical properties and thermal stability, while ensuring recyclability. Moreover, when specific fillers are used, the resulting composites can offer a variety of properties from electrical conductivity, to some degree of thermal conductivity, to magnetic properties, to increased UV and IR resistance[2]. Nevertheless, new green coating processes (as a green route to electroless plating) can insure a metal coating on plastic and composite components, thus protecting from radiations, allowing for thermal dissipation pathways, while offering superior electromagnetic properties.

Particularly interesting is the possibility of thermoplastics and their composited to be processed via Additive Layer Manufacturing (ALM), and particularly FDM, as it allows the in-space manufacturing, even in condition of microgravity. Moreover, the use of ALM allows to obtain a variety of complex shapes, optimizing the functions, while decreasing the weight [3].

Finally, it is important to mention the increasing importance, in the space colonization programs, of the ALM processing of metals, starting from polymeric composites precursor feedstocks, where selected metal powders are fastened together by a blend of organic binders, to form filaments to be processed via FDM. The printed part (called the "green") needs to be thermal treated in order to remove the binders (de-binding stage) and to sinter the metal particles to form a bulk metallic part [4].

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Stripping the primary coating layer from the fiber optic surface

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The fiber optic industry is developing year by year due to civilization progress demand. This means that fiber optic solutions have to be delivered faster and cheaper while maintaining a high level of the fibers quality [1]. Optical fibers are applied in many different applications in various environmental conditions, especially in communication and measurement systems, where the quality and speed of the transmitted signal is of paramount importance. Correct connection of optical fibers is a very important issue because it affects the quality of the transmitted signals. Connectorization requires high precision on each step of the technological process [2]. To meet these requirements all of existing methods of fiber stripping are time consuming and based on manually operated mechanical devices, where stripping elements are based on blades.

The presentation describes a new technology of thermal removal of the acrylic coating layer from optical fibers. In order to understand complexity of the process, the principles of glass fiber optics in terms of basic structure, main types of fiber optic tubes and cables, and finally fiber optic connectors will be described. The decomposition of the acrylic protective layer process has been analyzed in detail. The collected knowledge of the acrylic samples allowed to know the thermal properties of the tested material, design the stripping process strictly based on acrylic properties and allowed to achieve high efficiency of the designed process. Based on the analysis of the results of thermo-gravimetric tests, the decomposition temperature of the acrylic layer was determined, and then, knowing the optical and geometric parameters of optical fibers, a prototype of a device for the automatic removal of the protective layer from the terminal of optical fibers was built. The designed control system and the prototype of the device, which consists of a 6-axis robot, vision system and regulators, will be presented. It will be shown that it is be possible to remove acrylic layers much faster than before, while maintaining very good quality of optical fibers. Due to these advantages, the presented technology can be successfully used in industrial lines intended in the fiber optic connectorization process.

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[2] Connectors, https://ecatalog.corning.com/optical-communications/US/en/Fiber-Optic-Connectivity/Connectors/c/nav-connectors?productsSearchState=&resourcesSearchState=&relatedContentSearchState=&initialResultType=products&searchText=&, 2020 March.

Polymer hydrogels and their composites with nanostructured particles: from preparation to advanced applications

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In this talk, an overview of the research done in the Nanostructured Polymers and Gels Group regarding the development of polymer hydrogels and their combination with nanostructured particles (magnetic nanoparticles, polymer nanoparticles and others) will be given. Within this context, the employment of biobased polymers from renewable sources, mainly polysaccharide and proteins, to obtain functional hydrogels for advanced applications will be stressed. Different methods for the preparation of nanocomposite hydrogels will be presented including their employment as encapsulating matrix or as templates for the synthesis of metallic nanoparticles, combination with stimuli responsive hydrogels to obtain dual responsive interpenetrating polymer hydrogels or polyelectrolyte-based hydrogels and multilayer combinations obtained through electrostatic interactions. The influence of the structural organization of nanoparticles within the polymer hydrogels at different scales (nano, micro and macro) with emphasis in the determination of the rheological properties will be presented Finally, some selected applications, mainly in thebiomedical field (controlled drug delivery and hyperthermia) will be outlined.

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Organic photodetectors for NIR biological tissue window

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The organic photodiodes are the class of light photodetectors which are now investigated with an aim for applications in existing imaging technology, optical communication and environmental monitoring [1-3]. Nevertheless the photodetectors working in optical window of water (640-1300nm) are particularly desirable because of the possibility to apply them for imaging of biological objects or monitoring biochemical reactions [4]. Other sector strongly oriented on the development of the near infrared and infrared photodiodes is the sector of optical communication. Organic semiconductors are an interesting new group of electronic materials that combine some of the features of classical semiconductors with the chemical and physical properties typical of organic materials, including polymers. Their properties, such as their ability to absorb light or emit light in the desired spectral range and their electrical conductivity, as well as their solubility in organic solvents, facilitate their potential use in future electronic devices, which will be characterized by novel properties, such as light weight, flexibility, biocompatibility, biodegradability etc. [5].

The compounds with regularly alternating the D unit with the A unit along the polymer backbone are one of the most promising strategy in designing low bandgap semiconducting polymers. The driving forces between the D unit and A units facilitate the delocalization of *p* electrons and often change structure formation along the polymer main chain what leads to decreased bond length alternation and energy gap. The using of such type of materials,in photodetector active layer, allowto obtain remarkably high detectivity, exceeding 2×10^{13} Jones [6].

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Dispersion and electrical percolation of shortened carbon nanotubes in styrene-butadiene based blockcopolymers

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Aim of this research is the development of functional nanocomposites based on tough and flexible styrene-butadiene (SB) block copolymers (BCPs) with carbon nanotubes (CNTs) suitable for electrical and sensing applications. Due to their structural characteristics and interesting designable property profile BCPs offer high potential as template matrices for controlled and phase-selective incorporation of nano-scaled particles, as the nanofiller dimensions are in the range of the domain sizes of the block copolymers. For example, in SB block copolymer composites with oligostyrene-modified montmorellonite, it was possible to achieve a preferential inclusion of the silicate layers in the PS-rich phase, resulting in a mechanical reinforcement without reducing the toughness [1].Via selective incorporation of CNTs it is aimed to improve the mechanical properties of the BCPs and/or to introduce electrical conductivity, while significantly reducing not only the extent of filler incorporation but also the material costs compared to homogeneous filler dispersion within a polymer matrix.
MWCNTs can be dispersed very well in SB triblock and starblock copolymers without affecting the nanostructured morphology andwhile retaining the extraordinary mechanical property profile of the BCPs [2-4]. Melt mixed BCP/CNT composites exhibit high electrical conductivity at low CNT contents of ~ 1 wt % [2,3]. Composites processed by solution mixing are electrically conductive already at a filler content of 0.1 wt % [4]. To enhance the compatibility with the BCP phases MWCNTs were chemically modified with functional groups [4].The most significant challenge of using CNTs as nanofiller in BCPs is ensuring their sufficient dispersion and uniform distribution in the polymer matrix in spite of their high aspect ratio (length in micrometer scale) and intrinsic tendency to agglomerate.Therefore significantly shortened MWCNTs were used to ensure more favorable size ratios between nanotubes and block copolymer phases in order to increase the possibility of selective localization of the CNTs in one of the BCP phases.Different size fractions were realized by shortening the CNTs in a mixer mill. The BCP composites were prepared by solution mixing and melt mixing. The influence of the size fractions used on the morphology and the electrical properties of the BCP/CNT composites were analyzed.

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Synthesis of new nanocomposites based on magnesium and silicon by the combination of *in situ* sol-gel chemistry and reactive extrusion

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Commonly used nowadays, the sol-gel process is a method for synthesizing large number of products used in multiple applications. The method is based on a hydrolysis reaction of an organometallic precursor, such as metal or silicon alkoxides, followed by condensation reactions. The most widely used inorganic precursors are silicon alkoxides. The combination of different nature inorganic precursors is also the subject of studies leading to mixed oxides [1, 2] or nanopowders [3] formation.

Bearing this in mind, our work aimed to synthesize new compounds based on magnesium and silicon by sol-gel process. The emphasis was put on synthesizing products containing Mg-O-Si bonds. For this, two magnesiumprecursors, namely magnesium ethoxide and acetate were selected. Diethylphosphatoethyl-triethoxysilane (SiP) was identified as silicon precursor. The reaction between precursors was followed by TGA-GC-MS coupling, by XPS analysis and by a rheokinetic study. Consequently, the identification of the reaction by-products, the monitoring of the chemical crosslinking and the gelation of the reaction medium, as well as the appearance of Mg-O-Si bonds allow to confirm the reaction between precursors and to define the nature of formed products.Finally, these syntheses were transposed into a molten polymer medium using the reactive extrusion process.

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A novel, ultrathin2D-Like Polydopamine membranes from the Air/Water Interphase – tuning polymerization proces towards better understanding of their nanostructure

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Polydopamine (PDA) is a biomimetic polymer, first described in 2007 by agroup of scientists inspired by the mussel adhesive properties [1]. Since then, PDA has made a sizable impact in various fields, e.g. preparation of the Li-ions batteries, synthesis of antibacterial materials, biosensors engineering, molecular imprinting, tissue engineering, bioimaging, and finally photocatalysis [2-4]. PDA can be synthesized in a straightforward process of oxidative polymerization of dopamine hydrochloride induced by alkaline pH, most often achieved by the use of the Tris buffer solution [3, 5]. During the described procedure, three types of PDA can be formed, and each of them have a set of unique properties. They are namely: nanoparticles embedded in the solution, thin coating on virtually any type of substrate that is immersed in the solution, and the membrane at the air/water (a/w) interphase [6, 7]. Importantly, no membrane can be generated at the surface of a vigorously stirred solution. Therefore, appropriate soft-stirring conditions and constant oxygen inflow need to be applied to obtain membranes from the a/w interphase,showing the completely different structural and chemical character from the PDA generated in the bulk solution [8]. This year, our group have shown as the first an unknown laminar 2D-like structural ordering of these membranes [9]. That was of great importance, especially while taking into account their potential applications, e.g. construction of the new type of van der Waals heterostructures [10]. Unfortunatelly, to this date, there is no systematic and comprehensive study towards efficient production of these unique materials. Especially, any communication about their successful transfer onto functional substrate and broad characterization of such obtained heterostructure is not available. However, very recently, our group managed to obtain ultrathin membranes of a great homogeneity and wettability.Moreover, by using a novel spectroscopic reflectometry setup it was possible to observe their growth in situ and live. Therefore, in this study, several attempts were made to optimize the procedure by refining a transferring (scooping) technique and polymerization conditions i.e. time of polymerization and reagents concentration among others. The potential of the SR setup was further developed and applied. Morphological properties of the final membranes (thickness, roughness) were investigated by Atomic Force Microscopy **(Figure 1a)**. Moreover, structural studies have been carried out, namely Raman spectroscopy **(Figure 1b)** and X-ray diffraction **(Figure 1d)**. This research made it possible to optimize the morphological and structural properties of the obtained membranes, which present great quality of the surface without cracks and visible discontinuities **(Figure 1c)**. Finally, further optimized ultrathin 2D-like PDA membranes were obtained, which can be easily transfer onto desired substrate resulting in laminar PDA/semiconductor nanocomposite.

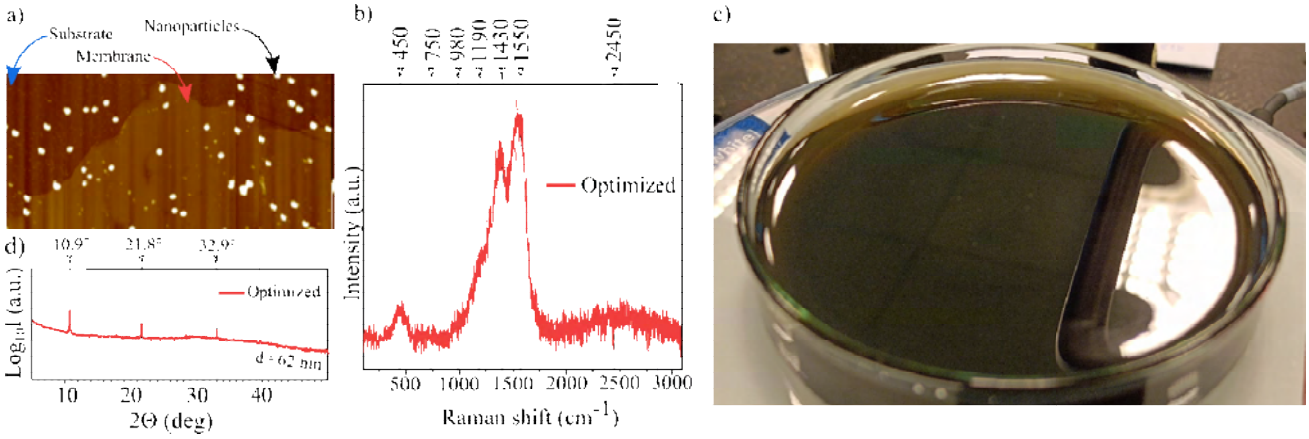

Figure 1: a) AFM image of the membrane transferred onto Si (100) substrate. b) Raman spectra of the optimized membrane. c) Surface of the PDA ultrathin membrane from the air/water interphase. d) Diffractogram of the optimized membrane revealed by the XRD.

Keywords: Polydopamine, membranes, structure, morphology, transfer

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LECTURES

TUESDAY, SEPTEMBER 28TH, WEBINARIUM

Synthesis of functional polymeric materials for optoelectronic applications

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The microelectronics industry and especially the organic/flexible electronics industry continue to demand new innovative polymeric materials. Examples of newly developed polymers of high charge mobility will be given as very promising, printable and stable active materials of printed organic field effect transistors (OFETs) [1]. Controlled polymerization techniques like Kumada-Catalyst-Transfer-Polycondensation allow to prepare polymeric semiconductors with precision structure under mild conditions with very low catalyst amount resulting in very high molar mass products with low defects improving performance. Donor-acceptor polymers have been fine-tuned in their electronic properties and microstructure by molecular composition design. Charge mobility in diketopyrrolopyrrole (DPP) polymers could be significantly increased by improving the synthetic procedures and film processing conditions [2].Also the issue of doping will be addressed [3].

Highly aromatic polymers exhibit usually high thermal and mechanical stability but also limited solubility and processability. Introducing branching can solve this limitation allowing to combining excellent material properties with the needed requirements for integration of these materials into application. Hb polyphenylenes prepared through Diels-Alder cycloaddition reactions have been prepared for their use as dielectric materials in MOFET as well organic field effect transistors. Highly soluble hb polyphenylenes of high molar masses could be prepared by the AB_2 approach.High refractive index (HRI) materials play a very important role in optoelectronic applications. E.g. aromatic HRI hb polymers have been developed based on an easily scalable A_2+B_3 approach making use of thiol-yne addition reaction. Fully soluble materials of reasonable molar masses and good film forming properties could be obtained which showed very high refractive index data up to 1.79 at 589 nm. High performance state-of-the-art phosphorescent red OLED external quantum efficiencies (EQE) of over 20 % having our hb polyvinylsulfides as polymeric out-coupling layer [4]. Thermally activated delayed fluorescence (TADF) materials are discussed as one of the most promising future OLED materials.(4-(3,6-Dibromo-carbazol-9-yl) phenyl)(4-(dodecyloxy) phenyl)methanone containing benzophenone and carbazole moieties was prepared in a straightforward synthetic way. Extension of the electron-rich carbazole-based system achieved through Yamamoto polymerization derived a clear TADF behavior with a photoluminescence quantum yield up to 71% [5].

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Application of polymers in solution processable organic electronic devices

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Over the last two decades, solution processable polymers, especially those containing a π-conjugated electron system or those possessing a high dielectric constant, have become increasingly important as functional electronic materials. Their applications cover several boosting industrial areas, namely:

(i) Flexible electronics, which refers to electronic systems that are assembled on a flexible substrate.

(ii) Printed electronics, where electronic circuits, including active electronic elements, are manufactured by printing technology, using mostly screen printing, ink jet, flexographic and gravure printing, suitable for a continuous manufacturing in a Roll-to-Roll (R2R) process. In the case of preparation of unstructured functional layers, slot-die, bar coating and knife-over-edge techniques provide thinner layers of higher homogeneity.

(iii) Organic electronics includes the field where the active electronic elements are formed by organic materials, such as polymer semiconductors, but besides polymeric also low-molecular weight materials are used. Besides printing, functional layers made of low-molecular weight organic materials can be prepared by vacuum deposition processes, which allow better controlling the process and, hence, the morphology of the layer.

(iv) Wearable electronics includes applications that are in direct contact with person. This area is mainly intended for applications enabling direct interactionwith body functions in various areas of human activities, such as professional clothing in the performance of high-risk occupations, leisure clothing in sports activities or home-care in the monitoring of sick patients. The aim is to integrate electronic systems directly into clothing so that they are as small constraints as possible for personal comfort. These applications are of significant importance in connection with the transfer of medical care to the so-called home care systems.

The currently prevailing trend is that purely printed or organic electronics is turning to the concept of the so-called **hybrid electronics**, which uses the advantages of different materials, organic and inorganic, for individual parts of the system for achieving the best desired functionality for the optimum price. By connecting silicon chips, printed silver paste conducting pathways and RFID antennas together with organic functional layers, it is possible to create, for example, smart RFID tags together with organic chemoresistive sensors, flexible OLED displays or OPV devices for IoT. Bioelectronic devices for monitoring and stimulation of cells prepared by printing techniques using organic semiconductors bring a number of advantages over conventional techniques, such as massive reduction in toxicity tests of new active substances, significant acceleration of results, study of the monitored response in real time, etc.When combined with organic thermochromic functional layers time-temperature indicators can be made, important particularly in food and pharmaceutical industryfor controlling “cold chain” during products transportation and storage. Suchdevicecould fill the gap between simple chemical indicators (price of few cents) and much more expensive full electronic dataloggers (several tens of EUR) Another need for dataloggers is for recording humidity changes where the dependence of the ionic conductivity of polymers on humidity can be exploited.

A currently emerging industrial field is**structural electronics**that involves printed electronic components and circuits that act as load-bearing, protective structures, replacing dumb structures such as vehicle bodies or conformally placed upon them [1]. This approach is often biomimetic.

Very interesting area of polymers application is in **memory devices**. The molecular flexibility of polymer chains and sidegroups allows switching between electronic states by various stimuli.Such low-cost flexible memory devices can be used for example, as a substitution of bar codes and security elements for the brand name products, or low-cost smart labels, which can record the violation of handling or storage conditions of sensitive products, and which would be much more difficult to counterfeit compared to conventional EAN or QR codes used today.In addition to their bi-stable conductivity some polymers show memristive behavior and are possible candidates for the neuromorphic computing elements [2].

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Investigation of molecular dynamics of poly(dimethylsiloxane) cross-linked by metal-ligand complexes by broadband dielectric spectroscopy

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Nowadays, flexible organic electronics hold a great potential in the "next generation" applications, such as foldable displays, wearable printable electronics, and advanced biomedical sensors. For that reason the elaboration of a fully stretchable polymeric dielectric materials and elevated value of dielectric permittivity for application in flexible electronics is very important [1, 2]. Implementation of described materials as dielectric layer for organic field-effect transistors (OFETs) could be the breakthrough for the development of flexible electronic devices. Polymeric materials cross-linked through dynamic non-covalent metal-ligand coordination (M-L polymers) are materials with significant potential to fulfill all described requirements.

In our work we focused on the poly(dimethylsiloxane) (PDMS) cross-linked by bipyridine-metal coordination (bpyPDMS-MeX_2). We systematically examined electrical properties as well as molecular dynamics by broadband dielectric spectroscopy for various M-L cross-linkers. Implementation of M-L coordination bonds into long PDMS chain improves the dielectric properties of this material because of the dipolar nature of the coordination bonds. The highest value of dielectric permittivity $\varepsilon' = 4.3$ (at 1 MHz) was noted for bpyPDMS-$ZnCl_2$ system, which is two times higher than for neat PDMS [3]. A direct correlation between the ε' and dipole moments of M-L bonds was shown by the density functional theory calculations. It was observed, that introduction of counter anions, which come form metal salt crosslinkers results only in slightly higher conductivity values of the materials in comparison to neat PDMS [4]. Furthermore, we demonstrated that the chemical incorporation of ligand moieties into polymer matrix suppresses PDMS crystallization. Two segmental relaxations α and α_{ac} were found and one of them comes from the lower mobility of PDMS chains, as they are immobilized by M-L coordination centers.

Results of our research showed that double-edged challenge was solved as we obtained dielectrics with elevated value of ε' without deterioration the non-conductive nature of the polymer.

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Nanostructured thin films obtained by dip-coating poly(butylene succinate), poly(ε-caprolactone) and their copolyesters (PBS-*ran*-PCL)

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Poly(ε-caprolactone) (PCL) and poly(butylene succinate) (PBS) are fully biodegradable aliphatic polyesters. They have attracted a great deal of attention for the development of biodegradable packaging and biomedical applications, such as implant devices, tissue scaffolds and wound dressings [1]. In this work, we prepared and characterized multiphasic thin films containing PCL, PBS and a PBS-*ran*-PCL random copolyester (COPOL) through sequential dip-coating in chloroform solutions of the polymers. All the polymers were synthesized in our labaccording to a method reported elsewhere [2, 3]. The preparation method resulted in thin films with varying compositions of PCL and PBS components depending on the initial concentration of the dipping solutions and the number of dipping steps employed for the preparation of the samples. Atomic force microscopy (AFM), grazing incidence wide angle X-ray scattering (GIWAXS) and scattering-type scanning near-field optical microscopy (s-SNOM) and Fourier transform infrared nanospectroscopy (nano-FTIR) were employed to characterize the films obtained [4].

The results showed that the crystalline morphology observed by AFM corresponds to that of the last deposited polymer. In the case of films for which the last deposited layer was PCL, diffraction peaks assigned to the semicrystalline structure of PCL were detected by GIWAXS. On the other hand, for PBS-ending films, s-SNOM phase images and nano-FTIR phase spectra were measured, revealing information about the infrared absorption and thus the chemical composition of the thin films and the nanoscale organization of BS and CL sequences. From the results obtained it was possible to conclude that the samples present a heterogeneously mixed chemical composition with nanodomain regions of varying PBS and PCL content resulting in a morphology similar to that exhibited by immiscible blends.

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Charge transport in organic semiconductors

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Organic semiconductors are used in optoelectronic devices, such as organic light-emitting diodes, organic and perovskite solar cells, and organic field-effect transistors. The performance of such devices depends heavily on charge injection and transport. In many cases, organic semiconductors exhibit highly unipolar charge transport, meaning that they predominantly conduct either electrons or holes. A fundamental question is what causes this unipolarity. We demonstrate that an energetic window exists inside which organic semiconductors are not susceptible to charge trapping by water or oxygen, leading to trap-free charge transport of both carriers. The implication for devices such as OLEDs, organic solar cells and organic ambipolar transistors is that the energy levels of the organic semiconductors are ideally situated within this energetic window. However, for blue-emitting OLEDs with a large band gap this poses significant challenge to remove or disable charge traps.

A-DA'D-A type acceptor based polymer solar cells

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Over more than two decades of research, polymer solar cells have achieved tremendous progresses in materials & device engineering and applications. For further advance, the power conversion efficiencies (PCEs) of polymer solar cells need to be substantially improved.

Inspired by the recent success in non-fullerene electron acceptors (NFAs), we have developed a design strategy defined as "A-DA′D-A" to obtain a series of high-performing NFAs [1-3], called as Y series. D = electron donor unit while A and A′ = electron acceptor unit. The key to this molecular innovation is introducing an electron-deficient moiety (A′) such as benzotriazole or benzothiadiazole into the central fused ring. Generally, these electron acceptors show extended absorption in the NIR region and provide considerably low energy losses in organic solar cells, hence having set new records for the certified power conversion efficiencies by National Renewable Energy Laboratory (NREL).

It is worth mentioned that our research on these newly designed electron acceptors has attracted extensive attention. For instance, the research paper on the Y6 acceptor (Joule, 2019, 3, 1140) was cited over 1000 times by the others within a very short time since its publication. More importantly, the certified power conversion efficiency of more than 18% has been reported by our fellow researchers based on the commercially available Y6. The underlying role of these acceptors has been actively investigated at home and abroad. While first achieving the 15% PCE in the single-junction polymer solar cells, Y6 appears to be a universal electron acceptor and contributes to developing semi-transparent and flexible polymer solar cells.

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Molecular brushes used as templates for titanium dioxide nanoparticles synthesis

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Molecular brushes are very interesting group of the materials, providing a broad range of potential applications. They are the grafted polymers that are composed of many polymer chains (side chains) attached to another polymer chain (backbone). The most important parameters of molecular brushes are the grafting density (which defines how many side chains occur per one unit of the backbone) and degree of polymerization (DP) of the side chains and the backbone, respectively. Molecular brushes with precisely tunable composition of the backbone and the side chains and well-controlled size can be synthesized using ATRP (Atom Transfer Radical Polymerization). Because of that molecular brushes, especially with block copolymer side chains, can be used as unimolecular templates for nanoparticles synthesis.

The aim of this work was to obtain nanoparticles with desired morphology (size and shape) through the design of the template and usage of different precursors. Titanium dioxide nanoparticles were synthesized within molecular brush template. The polymer templates were prepared via ATRP using grafting from approach. The side chains of obtained brushes were made of poly(acrylic acid)-*b*-polystyrene block copolymer. Four different precursors were used for the synthesis of inorganic particles; in particular obtained materials were characterized using transmission electron microscopy, scanning electron microscopy, thermogravimetric analysis and viscoelastic properties analysis.

Acknowledgements: The authors thank to National Science Centre, Poland for the financial support through MAESTRO project, number UMO-2014/14/A/ST5/00204.

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One-component cationic photoinitiators for preparation semiconductor nanoparticles filled photopolymer composites

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The preparation of polymers with the addition of a substance that allows changing the final product properties has drawn attention in recent years. One of such additions are nanoparticles of metal oxides which are used as fillers. Fillers allows improving various properties, e. g. resistance to scratching, abrasion, heat, and other mechanical properties [1]. An example of such filler may be silica particles which can be modified with different substances. That provides a good base for obtaining materials with individual properties, e. g. either hydrophilic or hydrophobic. In this way we obtain, the possibility to change the prepared material's properties in the desired way [2].

On the other hand, zinc oxide is excellent reinforcement for polymers due to high-quality dispersion, low tendency to form large aggregates, and oxidizing solid power [3, 4]. Due to its good photocatalytic properties, titanium oxides are used very often. In addition, they have antiseptic and antibacterial properties as well as are chemical inert [5]. In addition, using metal oxides nanoparticles in polymer composite preparation can lead to a higher photo-curing rate and a better conversion degree [6,7].

Our work conducted pilot studies investigating the possibility of using our highly efficient one-component coumarin-based cationic photoinitiators (Sylanto®) [8]. The impact of silica/zinc/titanium oxide nanoparticles, in different ranges, on the behavior of typical representative epoxy monomer - 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE), and vinyl monomer - tri(ethylene glycol) divinyl ether (TEGDVE) was tested. The main advantage of using one-component coumarin-based cationic photoinitiators is the possibility to test the process at UV and visible light ranges (up to 405 nm) where commercially available iodonium salts do not show activity. Real-time FT-IR was used to control the effect of metal nanoparticles on the monomer conversion rate during irradiation, where using coumarin-based iodonium salts as photoinitiators allows obtaining highly reactive systems.

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Nanomaterials for biomedical applications

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Nanotechnology became an important field for biomedical applications [1]. Especially, development of specifically designed "smart" nanomaterials contributes to the targeted therapy and diagnostics of the diseased tissue. This approach is realized by incorporation of active ligands on nanoparticle (NP) for recognition of biological receptors [2]. Large surface areaof NP's provides an excellent platform for their functionalization that may result in fabrication of various possible multimodal nanoplatforms [3].Multimodality may cover higher generations contrast agents, such as superparamagnetic NPs, which while acting as contrast agents [4], can be utilized as drug-carriers,tools for localized hyperthermia or photodynamic therapy [5-8]. Furthermore, specifically designed nanomaterials can exhibit: a) desirable and controlled release profile of bioactive agents (coating chemistry), b) prolonged blood circulation time, c) improved delivery of therapeutics across biological barriers, and d) multiple receptor targeting. All above-mentioned features providing significant opportunities in nanobiomedical research will be discussed in this talk.

Acknowledgments
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Photocurable Resin for 3D Printing

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1. Introduction:

With the invention of the stereolithography method (SLA) in the 1980s, various three-dimensional Additive Manufacturing (AM) methodshave been invented and put into industrial use.Today, each fundamental patents' right has been expired after more than 20 years have passed and big turning point has arrived. Inexpensive Material Extrusion (MEX) type 3D Printer becomes very popular for engineer and hobbyist, and an opportunity for "New Manufacturing Era" has arrived.

Today, in order to promote Digital Transformation (DX) manufacturing, 3D printingisconsidered to be important and convenient with great expectations.

2. 3D printing:

The word "3D printer" is well known to elementary school students.3D printing is based on 3DCAD data, liquid photocurable resin, thermoplastic resin, plastic powder, metal powder, gypsum powder, sand, etc. are used, and laser beam, electron beam, melt-extruded InkJet, etc. are used to accumulatethem layer by layer, which is defined as Additive Manufacturing (AM).The device is often referred to as a "3D printer" in simple terms and the technology is called "3D Printing". Table 1 summarizes the 3D Printing technology classified by ASTM.

Table-1: Classified 3D printing methods

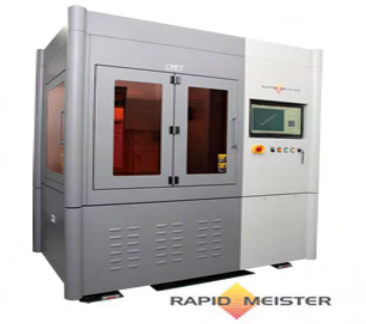
AM Process	Common name	Materials	Tool	Characteristics	Usage
Vat Photo polymerization	SLA	Photocurable resin	LASER, LED	Accuracy、Detailed Large size、	Prototypes
Powder Bed Fusion	SLS, SLM, EBM HSS	PA12powder、 Metal powder	LASER, Electron Beam	Products (PA, Metal)	Prototypes Products
Material Extrusion	FDM, FFF	ABS, PC Wire etc,	Heating	Easy, ABS ～ PEEK	Verification, High performance prototypes
Binder Jetting	Ink Jet, Z-Printer	Plaster、Sand Aqua binder	Ink Jet	High Speed, Full color	Figure Natural sand
Material Jetting	PolyJet, MJM	Photocurable resin	Ink Jet	Relatively easy Expression	Verification Expression
Sheet lamination	Sheet lamination, LOM	Paper, Plastic sheet	LASER, Cutter knife	Simple Full color	Stereo map
Directed Energy Deposition	LENS, DED	Metal powder	LASER	Metal	Metal parts
Hybrid		Metal powder Thermoplastic pellet	LASER + CNC Heat + CNC	Accuracy, Surface quality	Metal parts, Mold Large plastic parts

Materials for 3D printers range from gypsum powder, inorganic substances such as sand materials, metal powders such as steel, paper and resin powders to liquid photosensitive resins. These are used properly according to the needs of users, especially users in the industries, but from the viewpoint of the materials we get on a daily basis, each method is not yet in a sufficient performance. At present, users devise and use limited materials properly.

I have been engaged in 3D Printing field developing photocurable resin for VPP from 1991, in this lecture Iintroduce current status of 3D Printing and typical application of the VPP 3D printing.

2. VatPhotoPolymerization (VPP; stereolithography; SLA) method and its photocurable resin:

The VPP method is classified two types, one is "free liquid level type" irradiating 355nm laser beam from top area (Fig.1), and the other is "regulated liquid level method" irradiating laser beam (405nm) from bottom area (Fig.2) or irradiating UV/LED light by using DLP from bottom area (Fig. 3). Most of the low-price VPP equipment adopts this method because the system construction is simple.



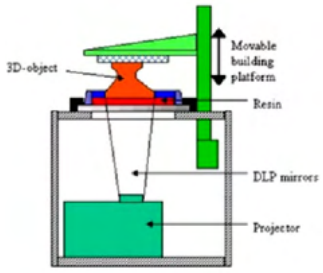


Fig-1: Large size laser VPP system

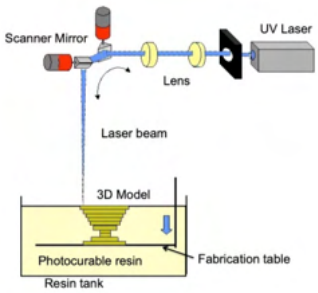


Fig-2: Regulated liquid type laser VPP system

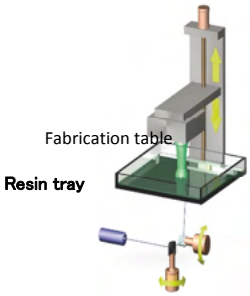


Fig-3: DLP type VPP system

The large-scale laser-type (free liquid level type) VPP systems is shown in Fig-1, in the resin tank it is commonly using a hybrid composition havingepoxy and acrylate compounds. On the other hand, "regulated liquid level method" type shown Fig-2 and Fig-3use (urethane) acrylate-based photocurable resins. The (urethane) acrylate-based photocurable resin is suitable for an inexpensive small-sized device because it has abundant compounds and cures with low energy as compared with the epoxy-acrylate based hybrid resin.

3. Application of 3D printing using photocurable resin:

The application of the VPP method is first of all, a man-machine interface for obtaining an industrial product from CAD data to a three-dimensional model, and tools and various simulations for efficient product development.It is to be used for industrial production.

The VPP method can give transparent, highly precise, high-definition fabricatedmodels.The typical application is; (i) prototypes for automobile industry and home appliances, (ii) making replica by silicone rubber mold with vacuum casting, (iii) and mold design supporting for injection molding of plastics and etc.Furthermore, the fabricated model is used for fittingand functional testfor prototyping, and has become an important tool for product engineering.

From the beginning of the invention of the VPP method, it is expected to makeactual parts, andthe target performance is ABS resin physical properties.But physical properties equivalent to ABS have not been reached at present.

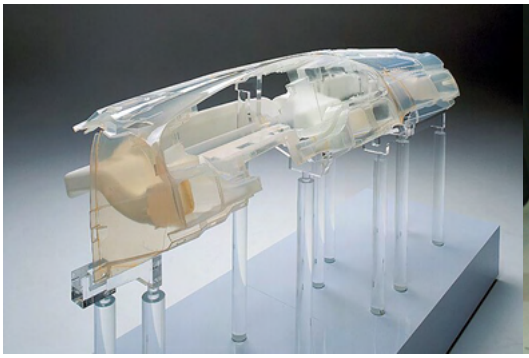


Fig-4: Prototype model

Fig-5: Functional test model

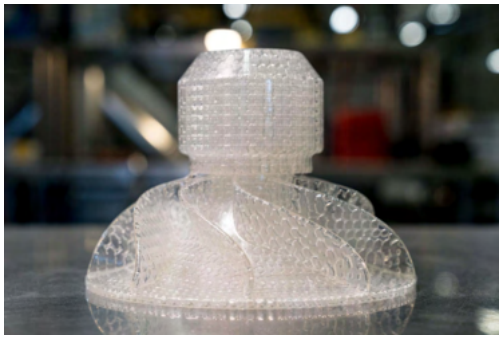


Fig-6: Casting model for burn-out

There is a big trend to make final products with 3D printers. However, the physical properties of the VPP method are not yet sufficient, there are currently only a limited number of examples of direct use for final products of industrial usage.

A typical example is the shell of a hearing aid with a DLP machine. Hearing aids have different ear shapes for each individual, so they are suitable for 3D printing based on CAD data in order to adapt them to each other.

In addition, jewelry applications for shaped objects have come to play a major role. 3D printing has made a breakthrough in jewelry production, which was mostly traditional manual work.

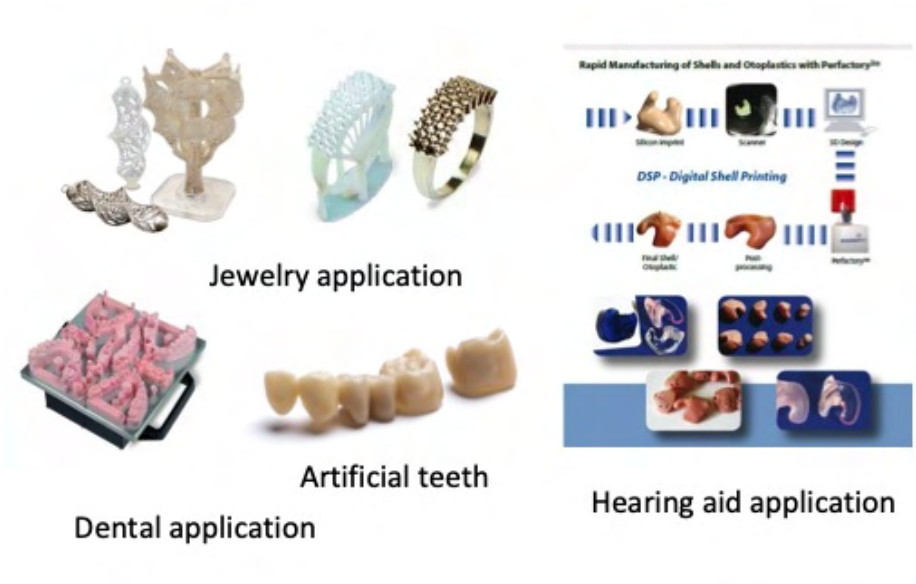


Fig-7: Typical application for jewelry, dental and hearing aid.

And the application of dentistry is advancing.Dentistry is the same size as the jewelry field, and many of the techniques cultivated in jewelry can be used.After outputting the data obtained from an intraoral scanner to STL format, by VPP systems (i) a wax pattern for casting, (ii) a casting pattern called a denture for castingand (iii) a tooth profile called a plaster model are created. It is shaped and used for dental purposes. In addition, the development of materials for directly modeling artificial teeth and orthodontic jigs (aligners) ideal for patients using data output by a three-dimensional intraoral scanner is also in progress.

In March 2015, “Carbon 3D, Inc.” (Now Carbon, Inc.) announced a high-speed laminated modeling process that uses a “Continuous liquid Interface Production (CLIP)”by continuous lifting process using DLP with a big topic. After the announcement of the CLIP method, many DLP equipment company developed same kind of the high speed systems. And the VPP method is drawing attention again. These are those that irradiate light in synchronization with continuous pulling, and although there are some restrictions on the

shape, it is possible to make model at a high speed several times higher than the conventional method, so attention is paid from various fields. Carbon,Inc., together with Adidas, developed the application to the bottom part of sports shoes and promoted the practical application to the final product. "Figure4" system of 3D Systems announces several resins that provide high-speed shaped objects with good physical properties that can withstand long-term changes of 5 years or more for use in final products.

Fig-8: Foot wear application

In response to the trend to manufacture final products with high-speed DLP machines, large European chemical companies are joining the material development one after another. BASF, Henkel and EVONIK are entering the market with their own photocurable resins.

4. New Application of VPP method using photocurable resin:

Lithoz, a venture company of the TU Wien in Austria, is promoting ceramic 3D printing with a bottom-irradiatingsystemusing DLP. On the other hand aSystem called "CeraMaker" from 3D Ceram-Shinto of France has been launched as a system to obtain a ceramic-containing model by using a bred paste-like resincontaining a high concentration of ceramic, and irradiating it with an 355nm ultraviolet laser. It has been developed into three-dimensional fabricating of various ceramics.

Adomatec of the Netherlands has put into a market with a device that applies a ceramic-containing photocurable resin on a PET film and irradiates it with light from the bottom surface using DLP.

The ceramic 3D printing using photocurable resin is becoming active, and it is considered to be a big market.

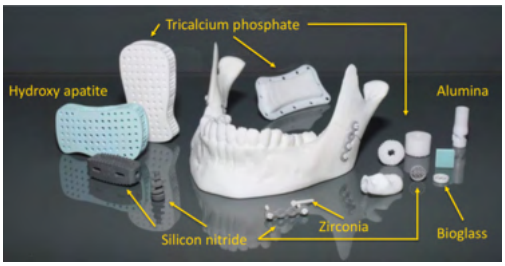


Fig-9: Ceramic application by Lithoz

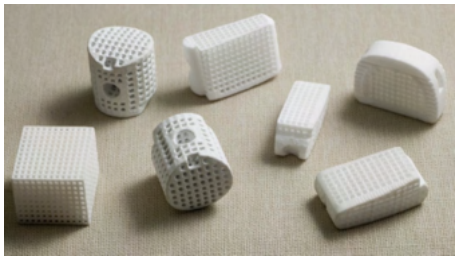


Fig-10: Hydroxyl apatite scaffold by 3D Ceram-Shinto

Fig-11: PTFE model by 3M

The Adomateccompany enables metal fabrication by modeling using metal fine particles instead of ceramics.3M is proposing the modeling of polytetrafluoroethylene (PTFE)using photocurable resin containing the powder.

5. Summary:

3D printing has the longest history, starting from the VPP method. The shaped objects obtained by this method cover a wide range from relatively large to small ones, and have high precision and high definition, and have made a great contribution to manufacturing in the industrial world. The physical properties of photo-

cured products (modeled products) have been developed withthe aim of ABS performance from the beginning, but have not yet reached that performance.It is being recognized that 3D printing will bring about a change in manufacturing, and the material development is attracting attention again.In particular, the development of materials for bottom-illuminated high-speed DLP machines is fierce, and it will be fully utilized as a final product in the very near future.It is expected that materials that can be produced will be developed. As a result, it is estimated that the VPP method, which specializes in high-speed, highly precise, and high-definition shaped objects, will contribute more and more to manufacturing.

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Enhanced antibacterial activity of polypyrrole with tunable conductivity, morphology and capacitance by acriflavine hydrochloride

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Polypyrrole (PPy) has been widely usedinbiomedicine including biosensors, tissue engineering and antibacterial applications, owing to its unique chemical and physical properties, environmentalstabilityand biocompatibility. Several efforts to enhance the antibacterial activity ofPPyhave been reported by the introduction of biopolymers such as dextrin, chitosan, gelatin or cellulose [1-4]. Also, metal or metal oxides have been used, however their high cost restrictthe potential biomedical applications [5-7]. Besides these, graphene, graphene oxide, carbon nanotubes, etc. have shown improved antibacterial properties along with promising capacitive properties in PPy [8, 9].

Recent studies revealthat the incorporation of organic dyes in PPy cantune the electrical conductivity as well as morphology of the composites [10]. Previously reported result by our group has demonstrated the influence of acid blue 25, for achieving elongated morphology,enhanced conductivity as well as the loweredcytotoxicity of PPy [11]. Nevertheless, the antibacterial properties of PPy in presence of organic dye was not studied, which inspired us to carry out the current research work.Herein, we report a simple and facile synthesis of PPyassisted by an organic dye, acriflavine hydrochloride (AF) to study the influence on the conductivity, morphology, capacitance and antibacterial properties. PPy was prepared by the oxidative polymerization using iron (III) chloride as an oxidant, in presence of different molar concentrations of AF. The yield of the resultant polymer was enhanced with the presence of dye. Also, the dye presence was confirmed using FTIR and Raman spectroscopies. The morphological studies indicated the conversionfrom globules to nanofibers when polymerized in presence of dye. The highest conductivity of 14.7 S/cm was achieved for the lowest dye concentrationas compared to pristine PPy which showed 1.1 S/cm.The very first-time effect of dye onthe electrochemical activity of PPywas investigated. The results demonstrated the enhanced gravimetric capacitance with the support of a dye. Further, the antibacterial assessment revealed an improved activity against both *S. aureus and E. coli* bacteria.The conductivity, morphology, capacitance and remarkable antibacterial properties of PPy controlled by an organic dye, allow applications wherever the electro-conductivity and antibacterial activity can be related, for example, wound healing, electrochemical sensors, bio-actuators or even regenerative medicine.

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Optically active nanocolloidal ink for 3D printing

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In the early 1980s, 3D printing proved to be a revolutionary manufacturing strategy that allows materials to be produced with preprogrammed complex shapes, morphologies, and compositions [1].
This work is aimed at creating optically active structures using extrusion 3D printing methods based on latex nanoparticles (NPs). Printed objects can be applied asanticounterfeiting materials and coatings. The novelty of this work consists in obtaining a new type of ink for 3D printing based on positively and negatively charged latexes.

Latex NPs were synthesized by emulsion polymerization of ethyl methacrylate with varying the nature of the initiator and surfactant to control the NP charge. The resulting ink due to the inclusion of dyes in latex NPsstructure based on anthracene (blue) and fluorescein (green) were able to emit light when irradiated with wavelengths of 380 nm and 480 nm, respectively.

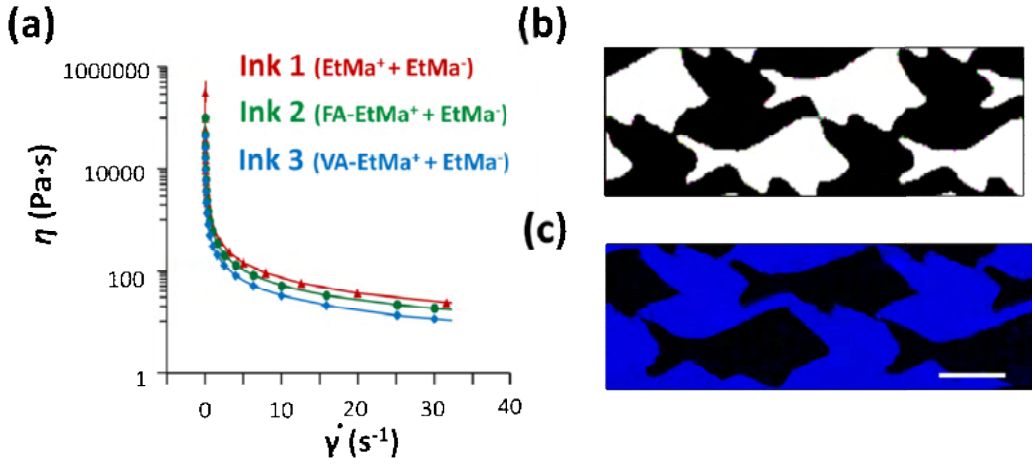

Figure 1:(a) Variation in complex viscosity, η*, of inks 1-3 in the gel state, plotted as a function of the shear rate γ; (b)appearance of the original Escher's Mauritz pattern (Sky and Water); (c) Escher's Mauritz pattern under irradiation with a wavelength of 375 nm (scale bar is 1 cm).

It was shown that mixing of positive and negative NPs in special ratio lead to formation of shear-thinning gel, which was proovedbt rheological measurements (Figure 1). By combining different inks (with and without dye) in one image,hiden in a day light images were printed, which could be revealed upon excitation withwavelength of the respective dye.

Thus, nanocolloidal ink based on oppositely charged latexes was obtained, the conditions of gelation were studied, the rheological characteristics were optimized and investigated, it was found that the obtained ink is capable of self-healing. Optical active structures have been obtained using 3D printing, studied the mechanical and optical properties of the printed structures. The shear thinning ability of ink and rapid viscosity recovery after shear stress holds great promise for its use in 3D printing.

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Building of polymer networks: focus on gelation phenomenon

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Computer simulations of non-equilibrium phenomena and complex polymer systems with cooperative dynamics

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Computer simulations play an important role nowadays in the process of gaining new knowledge, in addition to the theoretical and experimental approach. Theoretical considerations give a basis for simulation models,and the results obtained from simulation should alwaysbe compared with the experimental data. Studies of time-dependent phenomena and polymeric materials are particularly difficult because their properties usually involve a variety of time scales and a broad range of sizes. A lot of full-atom and coarse-grained computing methods exist for polymer studies, from quantum calculations, through molecular dynamics and ending on Monte Carlo methods, but all of them have limitations, along with hardware restrictions. The results are frequently focused on diffusive behavior, morphology, solvent dynamics, static properties, and properties of the controlled synthesis process of polymer macromolecules, all of them at the molecular level.

In this presentation, some exemplary results of the use of Dynamic Lattice Liquid (DLL) modelwill be demonstrated,a model originally proposed by T. Pakula [1] as a lattice Monte Carlo method thattreats matter as a coarse-grained system with realistic time scale. The survey will includesimulation results for various polymer systems and phenomena:static and dynamic properties of bottle brushes [2], polymer stars with highly compact multifunctional cores [3], polymer brushes on flat surfaces [4,5], polymer opposing brush structures and dynamics [6], precisely defined bottle brushesunder good solvent conditions that are directly compared with experimental studies [7], radical reaction kinetics in the synthesis of polymer networks using kinetically controlled radical polymerization.

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Polymer Architectures by Chain Walking Catalysis - Theory, Simulations,and Experiments

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Chain walking catalysis is an elegant approach to obtain dendritic polyethylenes by polymerization of ethylene and α-olefines with a "walking" Pd-α-diimine catalyst into a variety of complex branch-on-branch architectures depending on pressure, temperature, and olefine concentration. Coarse-grained Monte Carlo simulations utilizing the bond fluctuation model of the chain walking process (CW) are performed to investigate the influence of the walking mechanism on the polymer topology under various reaction conditions[1]. Depending on the walking rate w of the catalyst between reaction events two distinct regimes can be identified: For low walking rates w≈1 the structure growths with linear chain extensions (suppressed walker movement) with low amounts of side chains, whereas high walking rates w»1 promote random and isotropic dendritic growth of the molecule. The transition regime, see Fig. 1, is characterized by large amount of branched side chains reflecting a cross-over regime with linear global features and dendritic local sub-structures contrary to randomly hyperbranched growth. Indeed, the obtained CW structures show characteristics of disordered dendronized bottle-brushes controllable by the walking rate of the catalyst. The analysis of the topological properties, the radius of gyration, and the scattering function of the obtained CW structures emphasize the differences with other hyperbranched topologies. A generalized mean field model is applied, and is found in fair agreement with the simulation data describing the scaling relation of the different regimes. Additional simulations of linear chains, perfect tri-functional dendrimers, and randomly hyperbranched polymers under full excluded volume conditions support the unique structural features obtained by the CW process. The CW catalyst only operates in the universality class of linear and dendritic structures and can produce dendritic bottle-brushes in the transition regime and bear no similarities to randomly hyperbranched molecules. Indeed, the CW synthesis provides a powerful tool to create imperfect disordered dendrigrafts / dendronized polymers in a straightforward one-pot preparation setup, and can be tuned by external parameters to improve the rational design of a novel class of hyperbranched molecules.

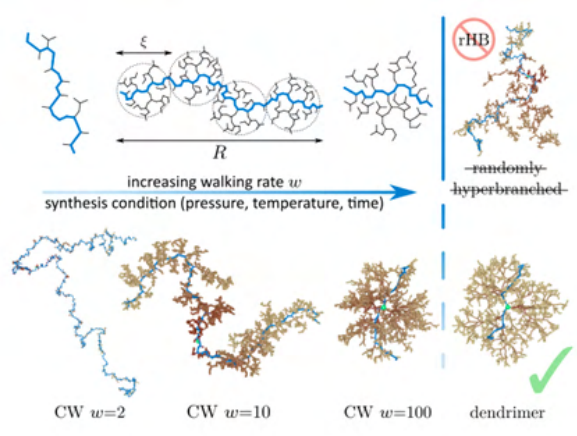

Figure 1: Sketch of the CW structures consisting of dendritic blobs and simulation snapshots for various walking rates depicting the transition process from linear to dendritic behavior. Reprinted with permission from [1].

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POSTER SESSION I

MONDAY, SEPTEMBER 27TH

Synthesis of branched polycaprolactone with mesogenic or photoactive macroinitiator

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Polycaprolactone (PCL) belongs to the group of biodegradable and bioresorbable polyesters with satisfied mechanical properties. Polycaprolactone is widely used as a biomaterial, but also to produce, for example packaging.

The reactivity of caprolactone as the monomer promotes the production of copolymers and the synthesis of PCL with different kind of initiators. Polymerization of caprolactone proceeds by ring opening polymerization, with addition of initiator, which may have a beneficial effect on the polymerization process and on product properties.

Numerous studies are carried out to check the course of PCL synthesis with initiators with hydroxyl and amine groups [1,2]. Poly(ε-caprolactone) and hyperbranched polymers (HP) are used in mutual modifications, as copolymerization reagents and also HP are used as initiators which is an innovative approach in research on these compounds. Branching of the polymer structure improves solubility, reduces viscosity and increases the amount of free functional groups, compared to linear polymers. Branched polymers are characterized by the ability to obtain higher molecular weights, and in many cases, increased mechanical strength compared to linear polymers [3]. Liquid crystalline compounds are an important group of chemicals with wide applications in the production of engineering plastics, electro-optical displays or liquid crystal thermometers they also have potential applications in the biomedical field [4, 5].

The synthesis of polycaprolactone was carried out using an organometallic catalyst and hyperbranched polyester with mesogenic or photoactive core as a macroinitiator. The macroinitiators used in the synthesis of PCL combines the advantages of hyperbranched polymers and liquid crystals which affects the obtainedatractive polymer properties. The structure of the polymer, its molecular weight and thermal properties were investigated by using low angle X-ray scattering (SAXS), size exclusion chromatography (SEC) and differential scanning calorimetry (DSC).

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Synthesis of poly (2-methacryloyloxyethyl phosphorylcholine) (MPC) for bioapplications

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Zwitterion compounds are a type of electrically neutral compound containing both cations and anions in their molecular structures (an equal number of positively- and negatively-charged functional groups). Besides, zwitterionic polymers, including polyampholytes and polybetaines, are polymers that consist of oppositely charged cationic and anionic groups along the chain or side chains [1,2]. In the first case, the zwitterionic electrolyte polymer has the same amount of positive and negative charges generated from different monomers. In the second one, both negative and positive moieties are presented within a single monomer, such as poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC).

Designing and surface modification of chemically, mechanically, or biologically suitable materials are important issues for preparation of new multifunctional biomaterials. MPC is used to synthesize polymer biomaterials with excellent biocompatibility which possess unique anti-biofouling properties with low friction abilities [3]. Additionally, PMPC-based materials applied in drug delivery systems are used for treating different diseases, especially cancer and pathogen infections.

In this study, a series of bottlebrush polymers based on PMPC were synthesized by atom transfer radical polymerization (ATRP) or reversible addition−fragmentation chain-transfer polymerization (RAFT) and used for lubrication and drug delivery systems. They were designed to interact strongly with functional groups of the cartilage surfaces or to interact and release drugs. Properties of synthesized polymers were characterized by gel permeation chromatography, GPC, nuclear magnetic resonance,^{1}H NMR and dynamic light scattering, DLS methods.

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The sensitization efficiency of photosensitizers for monitoring and acceleration of the cationic photopolymerization of monomers

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The quality of polymers obtained by cationic photopolymerization strongly depends on the extent of monomer polymerization. When the degree of cure of a polymer coating is too low, the coating is tacky; when it is too high the coating becomes too rigid and fragile. The degree of cure depends on a multitude of factors, such as the type of monomers, type and concentration of the photoinitiator, light intensity, irradiation time, temperature, moisture of the surrounding air, etc. Hence, precise control of the degree of cure is critical for photocurable coatings quality, while not many methods can be applied for that purpose. From among the methods used so far, Fluorescence Probe Technique (FPT) has been gaining increasing significance. The FPT method relies on the measurement of changes in fluorescence characteristicsof appropriate fluorescent molecular probes with changes occurring in the probe environment. The probes are added at small concentrations into photocurable compositions to sense the changes occurring during the polymerization process. However, the addition of any extra components to an existing formulation may be undesirable in some applications. In such cases, an ideal situation would be if a fluorescent probe could serve as both a cationic polymerization photoinitiator and a probe, or as a sensitizer and the probe simultaneously. Then, the photoinitiator or sensitizer used traditionally could be replaced with the dual-function component without the necessity of addition of any extra components. Unfortunately, the diphenyliodonium-photoinitiators do not fluoresce.

In this work, we present new compounds in the dual role: as fluorescent probes for monitoring cationic, free-radical and thiol-ene polymerization of monomers, and as sensitizers for the diphenyliodonium-photoinitiators. The research included the basic spectroscopic measurements, including, the measurement of emission and excitation spectra, fluorescence quenching after adding the photoinitiator in the form of the iodine salt, photolysis measurements and Real-Time-FT-IR and Differential Scanning Calorimeter tests. In addition, the new compounds are also suitable as fluorescent molecular sensors for monitoring and quality control of cationic, radical and thiol-photopolymerization processes using modern Fluorescence Probe Technology (in short FPT).

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Reversible brush polymers based on Diels-Alder reaction

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The smart surfaces are widely used in various fields as bioactive, sensory and antibacterial coatings for medical applications, catalysts for chemical synthesis, and hydrophobic surfaces for the fabric and glass industry due to variability of their properties. Under external stimulus such as thermal, chemical, electrical or optical these compounds can reversibly change physical properties. The introduction of reversible reactions for example the Diels-Alder reaction opens up a new way to control the functional properties of coatings. However, existing examples [1, 2] of reversible brush polymers based on the Diels-Alder reaction include the use of expensive organosilicon precursors or do not allow achieving superhydrophobicity(the contact angle with water is >150 ^{o}).

We have proposed the formation of the reversible brush polymersby the Diels-Alder reaction between maleimide fragments and furan groups contained in the polymer. For this purpose, furan derivatives containing the group $–(CH_2)_n$-Br (n = 2-4) will be obtained and used as modifierof polyurethanes containing tertiary amine.Additionally a number of N-Alk maleimide derivatives containing alkyl fragments of various lengths, including fluorinated ones will be synthesized (Figure 1).

The various length of the alkyl substituent in both furan and N-maleimide is needed for control coatings hydrophobicity.

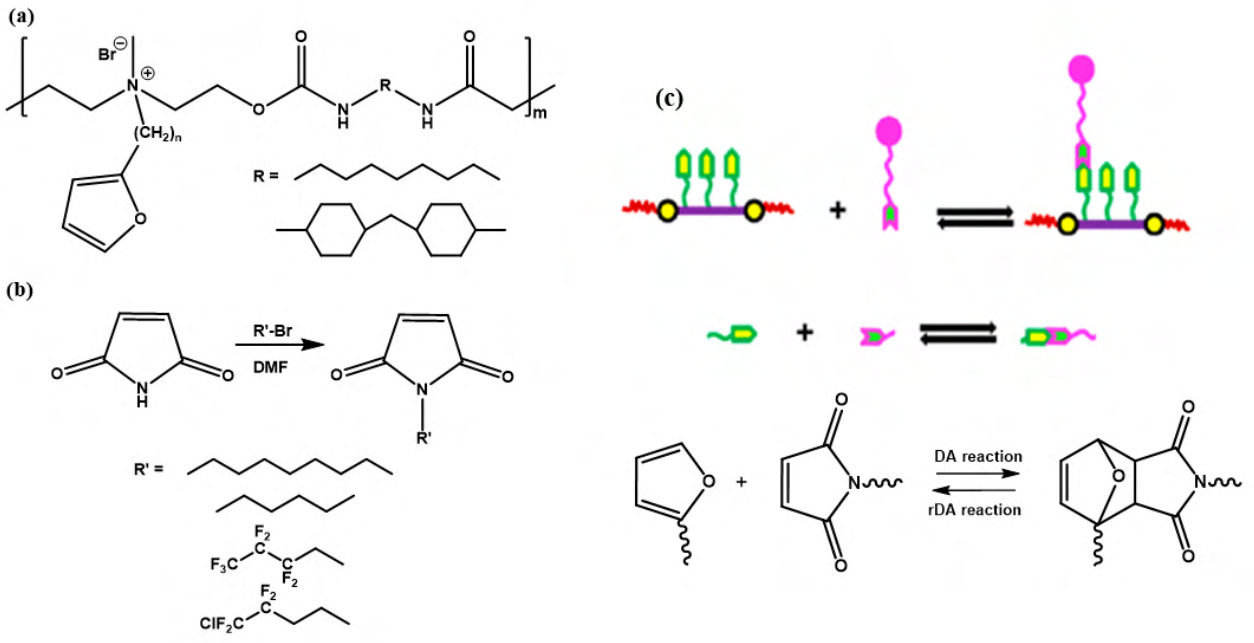

Figure 1. (a) Structure of polyurethane modified by furan fragment; (b) the scheme of the synthesis of alkylated maleimide derivatives; (c) the formation of polymer brushes by the Diels-Alder reaction

Acknowledgements: This work was supported by the Russian science foundation(Project No 21-79-20113).

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Micellar carriers based on choline grafted copolymers for antituberculosis drug delivery

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Drug delivery systems based on polymer nanocarriers allow for the enhancement of the therapeutic effect without increasing the risk of exceeding the toxic dose of the drug. There are various types of carriers, due to the polymer structure and way of the drug attachment. The structure of polymer have also a significant impact on drug release [1]. The copolymers with hydrophilic head and hydrophobic tail are able to self-organizing of their structure above the specific concentration, named critical micelle concentration (CMC) and forming a micelles. The encapsulation of drug inside the core is possible, due to their unique properties.Micelles for medical applications, can be made of numerous biocompatible polymers, both natural and synthetic. Choline derivatives seem to be good choice as co-monomers, because of their biological activities, which may increase therapeutic effect of the drug delivery system [2].

In present work the micellar carriers were based on ionic grafted copolymers, whichwere designed using a multifunctional macroinitiator, that ispoly((methyl methacrylate)-*co*-(2-(2-bromoisobutyryloxy)ethyl methacrylate)) (P(MMA-*co*-BIEM)) as the main chain and copolymer of methyl methacrylate and choline methacrylate (P(MMA-*co*-ChMA)) in the side chains[3]. Used copolymers varied with content ofChMA units (25% and 50%) and grafting degree (DG = 26% and 46%). The amphiphilic structure was proven by CMC determination (CMC=0.005-0.026 mg/mL). The process of self-assembly of graft copolymers with the addition of isoniazid, was carried out using the solvent method leading to the formation of micellar superstructures.Isoniazid was used as a model drug, because it is commonly applied in the conventional antituberculosis therapy as fist-line drug. The amount of encapsulated drug was verified by drug loading content which was determined with the use of UV-Vis (DLC = 15.0-78.7%). The*in vitro* release studies were carried for 48 h in PBS (pH=7.4, 37°C) resulting 16.4-94.9% of free drug. The present studies confirmed that the investigated grafted polymer systems are promising candidates as micellar carriers.

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A comprehensive analysis in one run – Conformation studies of protein-polymer chimeras

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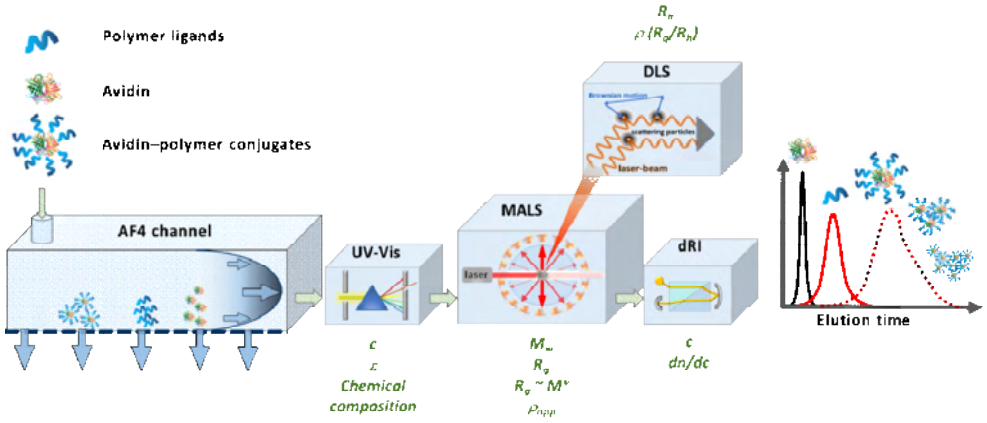
Polymer-based protein engineering has enabled the synthesis of a broad variety of protein-polymer conjugates that are widely applicable in therapeutic, diagnostic and biotechnological industries. Attachment of one or more polymer chains can prolong circulation time, increase stability and improve solubility of proteins. The synthetic advances can achieve the desired impact only if we can reliably characterize the conjugates. Some of the characterization techniques that are currently used include size exclusion chromatography (SEC) and dynamic light scattering (DLS). However, there are drawbacks associated with all these techniques that can result in incorrect evaluation of the prepared materials and do not provide an accurate understanding of sample's true nature.

Here, we demonstrate the advantage of asymmetrical flow field-flow fractionation (AF4) coupled to multidetection system for the comprehensive characterization of complex avidin-polymer chimeras [1]. This method allows for determination of intrinsic physical properties of protein-polymer chimeras from a single, rapid measurement. A library of protein-polymer conjugates varying in monomer and protein type, polymer grafting density and polymer chain length was analysed and a correlation of chemical and physical properties was demonstrated [2-4].



Scheme 1. Schematic representation of instrumental setup of asymmetric flow field-flow fractionation (AF4) with multidetection system for the in-depth characterization of molecular properties of avidin-polymer conjugates [4].

Acknowledgements: The authors acknowledge the grant HDTRA1-20-1-0014 for funding.

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Nanoparticles Obtained from Hydrophobically Modified Chondroitin Sulfate as Drug Delivery Systems

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Most of the chemical compounds used as drugs are hydrophobic,whichsignificantly reducestheir bioavailability in the human body. Drug carriers have been extensively studied for their ability to improve the pharmacological and therapeutic properties of conventional drugs.In recent years, polymers have become a very popular class of compounds used as adjuvants. Chondroitin sulfate (CS) belongs tonatural glycosaminoglycans (GAGs)that are present in the extracellular matrix and play a uniquerole in modulating cellular functions. Its biocompatibility and biodegradability properties make it very attractive for the development of nanoscale drug delivery systems (DDSs).

The purpose of our research was to prepare nanostructures from hydrophobically modified CS and determine their physicochemical properties. For this reason, several derivatives of CS were synthesizedby covalent attachment of octadecyl groups (C18) to the CS chains(Figure 1). The critical micelle concentration(CMC) values were determined for CSs with different degrees of C18 substitution. Then, dynamic light scattering and cryogenic transmission electron microscopy were used to obtain information on the size and morphology of the CS-C18 structures. The possibility of encapsulating of a model hydrophobic drug (curcumin) was also investigated.

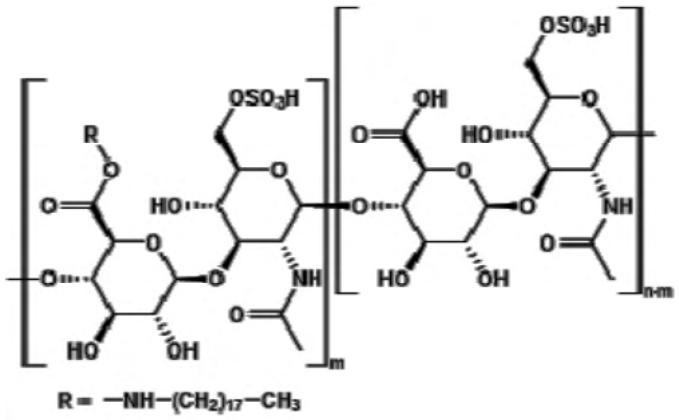

Figure 1: Chemical structure of CS-C18.

Acknowledgements: The authors thank to the National Science Centre Poland for the financial support (grant nr **2019/35/B/ST5/02147**).

Effect of temperature on free radical polymerizationof itaconic acid - quaternary ammonium salts melts

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Itaconic acid is a vinyl monomer of renewable origin, industrially produced by biotechnological methods. This makes itaconic acid an interesting substitute for petrochemically derived monomers such as acrylic acid and methacrylic acid. The free radical polymerization of itaconic acid gives the polyelectrolyte - poly(itaconic acid). However, so far known methods of polymerization of itaconic acid in both aqueous and organic solutions do not allow to obtain a polymer with a high average molecular weight, which Mwdoes not exceed 100000 g/mol)[1] .

A way to obtain poly(itaconic acid) with high molecular weight is to use an unusual reaction system, which contains an equimolar mixture of itaconic acid and choline chloride (quaternary ammonium salt) forming a liquid melt at room temperature - so-called Deep Eutectic Solvent (DES).[2] This type of mixture has similar physicochemical properties to ionic liquids and is considered a subclass of them.The characteristic properties of DES are high viscosity and low vapour pressure due tothe hydrogen interaction between mixture components.[3]The viscous reaction system affects the kinetics of free radical polymerization, accelerating the polymerization and increasing the average degree of polymerization of the obtained polymer.[4]

In this presentation, the preparation of poly(itaconic acid) with high molecular weight (Mw up to 350 000 g/mol) by photopolymerization in DES is presented and the effect of temperature on the polymerization process in DES is analyzed (Fig.1). The study shows that the high viscosity of DES (at mild temperatures) is the crucial factor to obtain poly(itaconic acid) with high molecular weight.

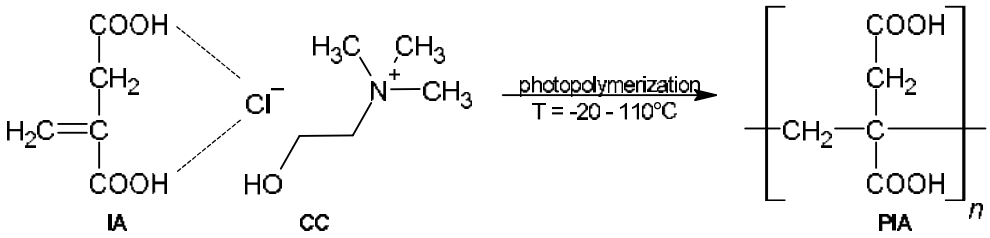

Figure 1: Scheme for obtaining poly(itaconic acid) (PIA)in Deep Eutectic Solvent composed of an equimolar amount of itaconic acid (IA) and choline chloride (CC)

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Comparative study on highly structurally similar trehalose and sucrose glycopolymers

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Trehalose-employing strategies gain particular attention in manyprotein related applications due to the great popularity of trehalose as an extraordinary protein chaperone, that is able to preserve protein structural integrity and to reduce aggregation of pathologically misfolded proteins.An approach, which were shown to stronglyamplify trehalose effectiveness is to create structures bearing its multiple copies.One important group of such highly functionalized multitrehalose structures, that has proved superior performance over molecular trehalose comprise its glycopolymers i.e. polymers with pending trehalose moieties.They have been successfully studied for many protein chaperoning applications that include:protein fibrillation inhibitors, excipients providing enzyme stabilization under stress conditions or allowing direct writing of protein patterns by electron-beam lithography, alternatives to PEGylation of therapeutic proteins as well as smart protein stabilizing and releasing nanogels. Trehalose incorporation has also been found to impair beneficial characteristic into macromolecular non-viral transfection agents of pDNA, cryopreservatives or hydrogel matrices for 3D cell culture. The action of trehalose glycopolymers is usually investigated in the context of structural differences in these macromolecules including the length of linker structure between trehalose and polymer chain, the way of trehalose functionalization, the position of functional group on trehalose, macromolecular topology, molecular weight or the ratio of sugar to non-sugar moieties. However, specificity of the action of trehalose glycopolymers is rather purely studied, as they are rarely compared with glycopolymers of other disaccharides. If so, they usually differ in the linker structure between disaccharide moiety and/or in the functionalization approach, what may significantly influence the overall macromolecule properties.

Herein, we provide the way for synthetizing highly structurally comparable trehalose and sucrose glycopolymers, which might be veryvaluable for deeper investigation of trehalose-containing macromolecules, especially to study their specificity or to unravel the mechanism of their exceptional properties, which has yet to be explained.The selected synthetic strategy is based on the Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization ofprecisely synthetized 6-*O*-acryloyl-trehalose and 6'-*O*-acryloyl-sucrose, which share several structural commonalities. They both have the same molecular weight and contain exactly the same number of hydroxyl groups, they are functionalised with acryloyl- functionality on primary hydroxyl group, they are non-reducing, and finally after being polymerised they both give polymers with terminal α-D-glucopyranosyl moieties.Importantly, employment of direct trehalose/sucrose acrylates for polymerization has the advantage of introducing just the short spacer between the main polymer chain and saccharide substituents, what furnish saccharide-rich macromolecules with very low content of non-saccharide parts. Both glycopolymers are comprehensively compared in view of their tendency to self-assembly, hydrolytic stability across wide range of pH and potential susceptibility to enzymatic hydrolysis by corresponding sugar hydrolases. Also, the biological availability of sugar residues on trehalose and sucrose glycopolymers is preliminary assessed, by testing their binding affinity towards Concanavalin A (ConA) – a lectin that is widely used to get first insight into biorecognition properties of glycopolymersbearing α-D-glucopyranosyl or α-D-mannopyranosyl residues. Finally, given the high potent of multitrehalose structures in protein chaperoning applications, trehalose glycopolymer is tested as potential inhibitor of amyloid fibrillogenesis of human recombinant insulinand the specificity of its action isthen verified by employing sucrose-containing counterpart.

Direct bioconjugation of α-chymotrypsin with thermoresponsive poly(*N*,*N*-diethylacrylamide-*co*-glycidyl methacrylate) copolymers: A route for enzyme-polymer nanoparticles with enhanced enzyme stability

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Responsive (smart, intelligent, adaptive) polymers have been widely explored for a variety of advanced applications in recent years. The thermoresponsive poly(*N*,*N*-diethylacrylamide) (PDEAAm), which has a better biocompatibility than the widely investigated poly(*N*,*N*-isopropylacrylamide) has gained increased interest in the last couple of years. In our work, the successful synthesis, characterization and bioconjugation of a novel thermoresponsive copolymer, poly(*N*,*N*-diethylacrylamide-*co*-glycidyl methacrylate) (P(DEAAm-*co*-GMA)) obtained by free radical copolymerization with various comonomer contents and monomer/initiator ratios are reported. It was found that all the investigated copolymers possess LCST-type thermoresponsive behavior with small extent of hysteresis, and the critical solution temperatures, *i.e.* the cloud and clearing points, decrease linearly with increasing GMA content of these copolymers. The P(DEAAm-*co*-GMA) copolymer with pendant epoxy groups was found to conjugate efficiently with α-chymotrypsin in a direct, one-step reaction, leading to enzyme-polymer nanoparticle (EPNP) with average size of 56.9 nm. This EPNP also shows reversible thermoresponsive behavior with somewhat higher critical solution temperature than that of the unreacted P(DEAAm-*co*-GMA). Although the catalytic activity of the enzyme-polymer nanoconjugate is lower than that of the native enzyme, the results of the enzyme activity investigations prove that the pH and thermal stability of the enzyme is significantly enhanced by conjugation the with P(DEAAm-*co*-GMA) co-polymer [1].

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Synthesis and Modification of Sugar-Derived Polymers for the Development of Sustainable Bioconjugates

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Bioconjugation, the attachment of biomolecules to synthetic polymers, produces novel, hybrid materials that combine the properties of each component, overcoming their limitations [1]. As such, bioconjugates are have become valuable materials, particularly in the field of healthcare – bioconjugaes are used astherapeutics,drug delivery systems and in bio-sensing [2] [3]. The vast majority of conjugates use poly(ethylene glycol) (PEG) as their synthetic polymer component. However, so called 'PEGylation' has several drawbacks. PEG does not biodegrade, so its conjugates can lead to bioaccumulation and toxicity [4]. PEG is also derived from fossil fuels. Therefore, alternative polymer components need to be found. The use of renewably sourced, biodegradable polymers is particularly desirable to alleviate the toxicity and environmental impact of bioconjugate design.

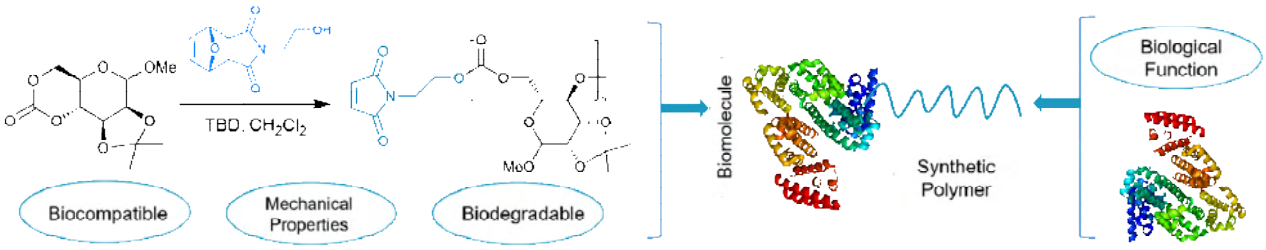

Figure 1. Bioconjugate design; attatchment of a maleimide-functional, mannose-derived polycarbonatewith a thiol-containing biomolecule.

Recently, several renewably-sourced monomers have been developed through the coupling of CO_2sugar derivatives [5-7]. The corresponding polymers are made by alcohol-initiated ring opening polymerization (ROP). The resulting polymers are degradable by hydrolysis to yield sugar diols and CO_2, and have potential to be both biodegradable and biocompatible. These properties make them ideal sustainable bioconjugation partners. This presentation will detail the synthesis and modification of such polymers to enable their employment as the synthetic component of bioconjugates. In particular, the use of a maleimide-functional initiator to produce thiol-reactive polymers will be highlighted. Post-polymerisation deprotection and conjugation of such polymers with simple thiols via Michael Addition chemistry will also be discussed [8]. Finally, work towards a bioconjugate with bovine serum albumin (BSA) as a model protein will be featured.

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Electrochemical characterization of saccharide-based copolymers in cell culture

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Electrochemical methods yield a vast amount of data regarding redox-active substances. However, they can be also applied for studying interfacial phenomena in much more complex systems than commonly used [1, 2]. Presence of insulating or conductive layers, their structure, chemical composition as well as their overall physical properties may change the parameters of the current flow.

In this communication we would like to present our recent research regarding electrochemical characterization of agar-agar (a mixture of agarose and agaropectin [3]), a saccharide-based copolymer of D-galactoseand 3,6-anhydro-L-galactopyranose /6-bisulfate-L-galactopyranose (**figure**) [4]. The scope of the research focused on construction of sensing system with electrical signal, that can be used for *in situ* measurements of the growth of the cells during cell culture studies.

The detection strategy will monitor the general changes in the current response of the system. In our research we studied the influence of density, layer thickness of the biopolymer as well as electrode substrate material on the electric response of the system. Not only we have fully characterized the electrochemical systems but also described phenomena corresponding to low ionic strength in the agar-agar modified electrodes.

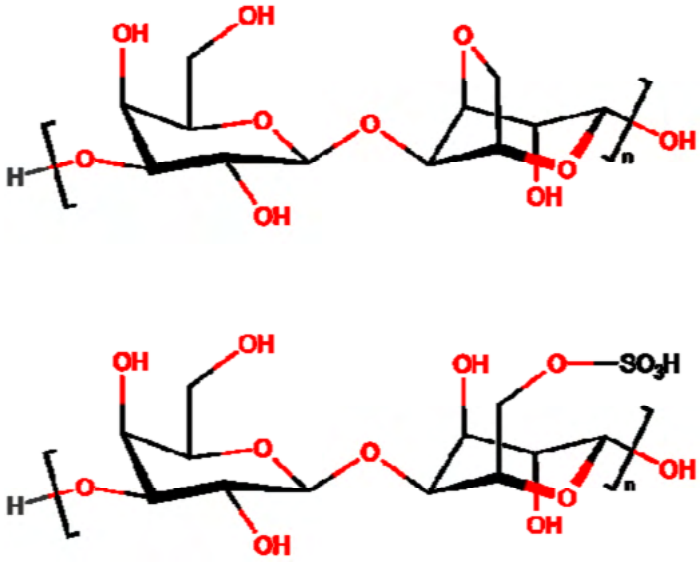

Figure: The structure of agarose (top) and agaropectin (bottom).

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Tunable Benzylidene Scaffolds as Efficient Chromospheres of One-Component Cationic Photoinitiators for 3D Printing Applications

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Recently, cationic photopolymerization meets with a growing interest, finding new applications in such areas as microelectronics [1], dentistry [2] and especially in 3D-printing [3]. These new applications create demand for new efficient photoinitiators.

One of the most active cationic photoinitiators are diaryliodonium salts which are characterized by good thermal stability, excellent solubility in monomers as well as low toxicity too [4]. However, most of commercially available diaryliodonium photoinitiators have poor absorption properties above 300nm what makes them inactive under common *Light Emitted Diodes* (LEDs) irradiation (especially maximum emission located at 365nm and 405nm). Very promising approach to overcome this drawback is to replace one of the aryl rings with more efficient chromophore like coumarin what improves absorption in near-UV region significantly [5]. This approach allows the iodonium salt to be photolyzed efficiently using LED emitted at 365nm and thereby generatessuperacid which initiates polymerization process of such monomers as epoxides, vinyl ethers, oxetanes and glycidyl ethers.

Here, we present a group of new one-component iodonium photoinitiators in which one of aryl ring was replaced by efficient chromophores based on benzylidene scaffold [6]. These chromophores containing extended conjugated bond system (double bond) and D-π-A structure exhibit push-pull effect which red-shifts absorption of their iodonium salts siginificantly and make them active under 365nm LED and in some cases under 405nm LED irradiation. Use of easily modifiable scaffold allowed to prepare 14 new iodonium salts with different properties what makes the possibility for analyzed effects of each modification on iodonium salt photoinitiating properties.

Photochemical activity of presented new iodonium photoinitiatorswas investigated in terms efficiency of photolysis (steady-state photolysis) andquantum efficiency of superacid generation. Their photoinitiating properties were analyzed performing photopolymerization test using *real-time* FT-IR technique. Photopolymerization process of 25μm thick coatings containing epoxide or vinyl ether monomers and tested iodonium salt (in 1% wt. concentration)was analyzed. Most efficient photoinitiators were used in 3D printing application tests with epoxide and oxetane monomers. They allow to obtain prints with desire spatial resolution under 365nm LED irradiation. Some of chromophores used in presented iodonium salts exhibit increase of fluorescence intensity in course of coating's irradiation. This effect can be used for photopolymerization process *on-line* monitoring. Therefore such designed compounds can be used as fluorescent sensors what is their additional advantage.

Acknowledgements: The authors are grateful to the National Centre for Research and Development (Warsaw, Poland) – INNOCHEM project contract number POIR.01.02.00-00-0038/16-00; project title: "A new generation of photoinitiators for photopolymerization processes dedicated to the coating-forming industry and adhesives."

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Thermoplastic binder systems-based 3D printable highly filled filaments for fused filament fabrication

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Fused filament fabrication (FFF) or material extrusion with filaments is one of the worldwide most commonly used additive manufacturing (AM) techniques, specifically when dealing with thermoplastic composites and polymers [1]. This techniquecompares to other AM processes, requires a very low initial investment and shows a short processing time, less material wastage, an easy operating system, reasonable control on processing parameters, also the possibility to use several materials simultaneously (multi-material 3D printing) [2, 3].

In this work, thermoplastic organic binders were compounded with highly metallic powder-loading to develop a feedstock. The binder provides the mechanical interconnecting of the loose particles to provide enough final strength to sustain throughout the processing. The feedstock prepared for FFF is similar to a highly commercial manufacturing technique called metal injection molding (MIM), where the green parts have 30-45% of binders[4].The study aims to developfilaments of highly loaded metallic fillers that can be successfully printed via fused filament fabrication (FFF).In this work, compounding of feedstock material with 55 vol.% copper and three distinct multi-component binder systems was done. The mechanical properties of the highly-loaded developed filaments were studied to ensure quality and printability. The study also compares the physical properties of the developed feedstocks.Finally, the parts were 3D printed to study the quality and printanbility of the highly loaded copper-based feedstock filaments.

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Optimization of polysaccharide based bioinks for 3D extrusion bioprinting

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3D Bioprinting is an innovative technique that allows the creation of three-dimensional scaffolds for tissue engineering and regenerative medicine. This technology employs a material known as "bioink" to create 3D structures in a layer-by-layer manner. Typically, bioinks are made of hydrogels (3D networks of crosslinked polymer chains) which offer an ideal environment for cells due to their hydrophilic nature and high water content, having at the same time, the elastic properties of a solid that can mimic those exhibited by natural tissues [1]. Nonetheless, there are a limited number of suitable hydrogels that can be formulated as biomaterial polymer inks (bioinks) and tuning their rheological properties for 3D extrusion printing remains a challenge [2]. In this study, a common desktop 3D printer was transformed into a low-cost 3D bioprinter. The pieces needed for the transformation were printed with the original desktop 3D printer. Using this lab-madebioprinter, different alginate-cellulose bioinks were optimized and used to print three-dimensional structures.The natural polymer alginate was chosen as the main component of the scaffold due to its tunable mechanical properties, rapid gelation and non-toxicity [3-5]. Microcrystalline cellulose was added to the hydrogel to modulateits mechanical properties for printing. The rheological properties (shear thinning behavior, gelation time, recovery time and elastic properties after build up) of these alginate-cellulose bioinks were assessed.A thorough discussion of their rheological properties was performed and related to their printability in the lab-made 3D extrusion printer.

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Investigation of $PEG_{8K}DMA/PEG_{100K}$ Solutions and their semi-IPN Hydrogels for Advanced Inks in 3D-Printing

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3D printing as a manufacturing strategy experiences increased attraction in a large number of applications, including tissue engineering. A potential bioink is composed of a hydrogel precursor providinga biocompatible, 3D tissue-like microenvironment, and potentially living cells. For a successful tissue reconstruction, a printable bioink should fulfill optimized rheological requirements as well before as after the printing process.

The employment of bimodal functional polymer solutions as precursors based on poly(ethylene glycol)s, and their photoset into semi-interpenetrating networks (semi-IPNs) (s. Figure 1 a)is our strategy to independently tailor the flow viscosity of the ink, as well as the mechanic properties including modulus, toughness and viscoelasticity, and swelling behavior of the resulting hydrogels.

Thereby, photopolymerization makes the bridge between the bioink solution and the 3D printed hydrogel object.The use of photopolymerized hydrogels as opposed to physical gels also allows for the material properties to be more easily tuned. Poly(ethylene glycol) dimethacrylate (PEGDMA) chains can be photopolymerized to form hydrogels in a controlled way. While the mechanical properties of the gels can be tailored by variation of the concentration of a functional poly(ethylene glycol), the viscosity and homogenous flow of the bioink is provided by a high molar mass polymer. Thus, semi-IPNs can overcome the difficulties of conventional hydrogel precursor solutions, and investigate the context of appropriate polymer concentration and crosslink density [1].

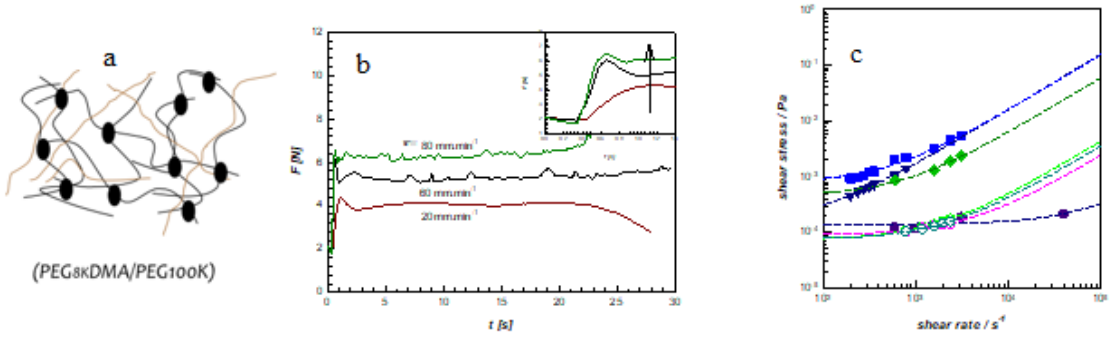

Figure 1: a) Semi-IPN structure of $PEG_{8K}DMA/PEG_{100K}$. b) Capillary extrusion graphs of functional aqueous $PEG_{8K}DMA$ solution (μ=20 m-%) at different velocities.c) Shear rate dependent viscosity characterization of $PEG_{8K}DMA/PEG_{100K}$ solutions and melts in capillary extrusion experiments.

In order to optimize structure-property relationships of bioinks and resulting gels, we use methodology such as rheology, capillary extrusion and mechanical tests. From this, we in particular investigate the viscosity, the shear-dependent flow characteristics, nozzle relaxation, and shear modulus of the inks andprinted hydrogels. The goal is to set the mechanical conditions and optimize fidelity and resolution of the printed formation after photoset, since each hydrogel-based fabrication system has different fabrication parameters. Experiments of capillary extrusion rheometry show that semi-diluted solutions and melts of $PEG_{8K}DMA/PEG_{100K}$behaveas non-Newtonian fluids.The presence of a yield stress isobserved that controls the flow and collapse of fluids.In semi-diluted solutions of $PEG_{8K}DMA/PEG_{100K}$we investigate their viscoelasticity and stress relaxation by varying of extrusion velocity and composition.Further,the zero shear viscosity of the hydrogel solutions are obtained between 0.03-10 Pa.sby oscillatory rheometry. On the semi-IPN $PEG_{8K}DMA/PEG_{100K}$ hydrogelsobtained by photopolymerization, we find that the swelling ratio, storage and loss modulus of synthesized hydrogels are highly favorable to advanced 3D printed tissue bricks.

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Modulus of the amorphous phase of semicrystalline polymers

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Mechanical properties of semicrystalline polymers are a derivative of a relative content of the crystalline/amorphous components and their individual properties. In most studies the influence of parameters of crystalline phase, such as the degree of crystallinity, thickness of lamellae or crystals orientation, on the mechanical response of semicrystalline polymers was analyzed and the role of those parameters was clearly defined.[1]The role of the amorphous component in the mechanical properties of semicrystalline polymers is less well characterized. Due to its irregular structure, mechanical properties of amorphous phase cannot be either measured or easily estimated. Some researchers have assumedthat the mechanical properties of interlamellar amorphous phase are similar to bulk rubbery amorphous phase. However, the mechanical properties of the amorphous phase confined between crystals can be significantly different from the bulk rubbery amorphous phase. The only one known experimental study which allows to estimate a value of the modulus of interlamellar amorphous phase of semicrystalline polymer (polyethylene) has been presented by Xiong et al. [2]. The obtained values of the modulus of interlamellar amorphous phase were 1-2 orders of magnitude higher than the values characteristic for the bulk rubbery amorphous phase. The method presented by Xiong et al. had, however, several disadvantages: dedicated to polyethylene only, access to unique experimental techniques was required.

The aim of our research is to develop a universal method to determine the modulus of interlamellar amorphous phase of semicrystalline polymers.The basics of the method were presented on the example of high density polyethylene (HDPE).To determine the value of the modulus of the interlamellar amorphous phase, a selective deformation of the interlamellar regions (by changing the distance between adjacent crystals, as schematically shown in Figure 1) was performed and then the value of the local strain/stress generated in the amorphous phase was measured.

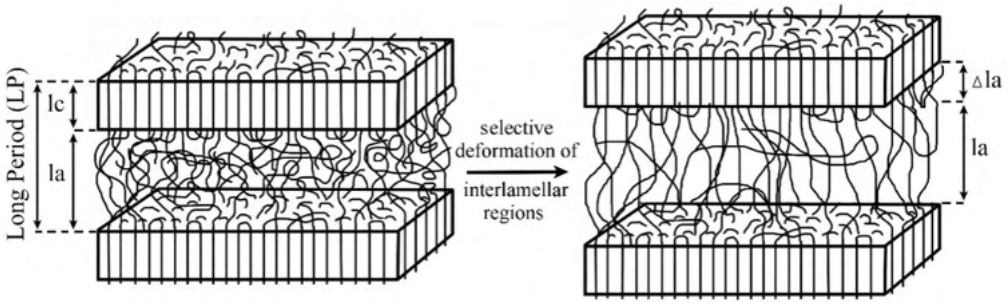

Figure 1. Schematic change of interlamellar distance.

The local deformation of the amorphous component was induced by the introduction of the swelling agent (hexane). The swelling-induced local strain and local stress of the interlamellar amorphous phase were estimated based on the changes of the long period and the yield stress, respectively. The determined modulus of the interlamellar amorphous phase of HDPE (≈40 MPa) was an order of magnitude higher than the modulus of the bulk rubbery amorphous phase of HDPE (≈3 MPa). The method was then applied to other semicrystalline polymers: low density polyethylene (LDPE), ethylene-octane copolymer (EOC) and polypropylene (PP) and their modulus amounted: 11.8, 4.2 and 50.3 MPa, respectively. It was observed that for polyethylene materials(HDPE, LDPE, EOC), the modulus of interlamellar amorphous phase increases linearly with the degree of crystallinity. For the polymer with the lowest degree of crystallinity (EOC, 26.2%), the value of interlamellar amorphous phase modulus was similar to bulk rubbery amorphous phase modulus. That led to conclusion that the influence of lamellar crystals on the stiffness of amorphous phase was low in that case.

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Copolymers of 2-isopropyl-2-oxazoline and 2-ethyl-4-methyl-2-oxazoline as alternative to poly(2-isopropyl-2-oxazoline) with reduced ability to crystalize

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Thermoresponsive polymers exhibiting phase transition around body temperature have attracted great attention due to their potential biomedical application. Poly(2-isopropyl-2-oxazoline) (PiPrOx) is well known among thermoresponsive polymers with a lower critical solution temperature (LCST) at physiological level[1], moreover it is nontoxic toward variety of cell lines [2-4]. Another unique feature PiPrOxis its tendency to crystallize uponthe prolonged incubation at an elevated temperature and the formation of hierarchicallystructured objects [5,6]. However, this property seems detrimental for certain, mainlybiomedical, applications.

Therefore, the aim of the presented work was to synthesize copolymers of 2-isopropyl-2-oxazoline and 2-ethyl-4-methyl-2-oxazoline in order to examine whether the presence of alkyl substituents randomly distributed within the main chain of a 2-isopropyl-2-oxazoline-based copolymer will decrease its ability to crystallize compared to its homopolymer.The thermoresponsive behaviour of the copolymers in water, the influence of salt on the cloud point, the presence of hysteresis of the phase transition and the crystallization ability in a water solution under long-term heating conditions were studied by turbidimetry. The ability of the copolymers to crystallize in the solid state and their thermal properties were analysed by differential scanning calorimetry and X-ray diffractometry. A cytotoxicity assay was used to estimate the viability of human fibroblasts in the presence of the synthesized polymers.

On the basis of the obtain results we can conclude that obtained copolymers of 2-isopropyl-2-oxazolineand 2-ethyl-4-methyl-2-oxazoline are nontoxic alternative to PiPrOx with a LCST close to the body temperatureand a greatly reduced tendency to crystallize.

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Block copolymers of β-butyrolactone and oxiranes –relationship between structure and properties

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Aliphatic polyesters are widely applied among others in medicine and pharmacy. The main application in this area is the production of biodegradable implants and sutures for surgery and also materials for tissue engineeringand drug delivery systems [1-3]. One of the important polyesters, belonging to the group of polyhydroxyalkanoates is poly(3-hydroxybutyrate) (PHB).PHB, also referred as bacterial, is isotactic poly([R]-3-hydroxybutyrate) and it serves as a storage material of carbon and energy in microbial cells. The ultimate PHB degradation product – hydroxybutyrates, are naturally present in living organisms, including mammalian blood [4]. Good biocompatibility, non-toxicity of degradation product make PHB as a particularly attractive material. PHB is also hydrophobic and the hydrolytic degradation proceeds on the surface, takes quite a long time and is difficult to control [5]. The synthetic analogue of bacterial PHB is the amorphous poly(β-butyrolactone) (P(β-BL)). However, similarly to PHB poly(β-butyrolactone) is also hydrophobic, degrade relatively slow, and the lack of functional groups limits its modification. Therefore, in order to tune its properties - amphiphilicity and biodegradation rate, P(β-BL) needs to be modified by copolymerization with other hydrophilic monomers or by introduction of functional reactive groups.

The aim of presented work is the synthesis of modified poly(β-butyrolactone) by block copolymerization with hydrophilic and also biocompatible oxiranes (glycidol (GL) and ethylene glycol (EG))of different lengths and arrangement of P(β-BL), PGL and PEG blocksand investigation the relationship between the structure of the obtain copolymers and their properties. Copolymers with the block arrangement as AB, ABC, symmetrical ACA and also ABCBA were synthesized via anionic ring opening polymerization using sequential monomer addition technique. The respective blocks are A - poly(β-butyrolactone), B - polyglycidolC - poly(ethylene glycol). For selected block copolymers the solubility in water and other solvents, glasstransition temperature, morphology, the philicity of their surface and degradation rate were investigated. Based on obtained results we can conclude that it is possible to control the properties of such copolymers by precisely selecting the length ofindividual blocks of different character (hydrophobic P(β-BL), hydrophilic PEG and PGL)The correlation of data obtained from the determination of the copolymer structure, properties and rate of degradation allow to obtain materials designed to specific applications.

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Additive manufacturing with photocurable liquid isoprene rubber

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Rubbers are an essential part of our daily life. Due to their unique material properties such as high elasticity, strength and recovery, diene-rubbers are applied in a vast amount of everyday products includingtyres, gaskets or sealants. In general, rubbers are crosslinked in a process called vulcanization, which can be thermally initiated either in the presence of sulfur or peroxides. However, novel routes towards the photo-crosslinking of diene-rubbers have been approached over the last years.[1]Photo-crosslinkingallows the curing of liquid diene-rubbers, such as liquid isoprene rubber, in the presence of light, which makes them interesting candidates for additive manufacturing like digital light processing (DLP) 3D-printing. DLP offers distinctive advantages including high resolution and surface quality at low cost and comparably high throughput rates.

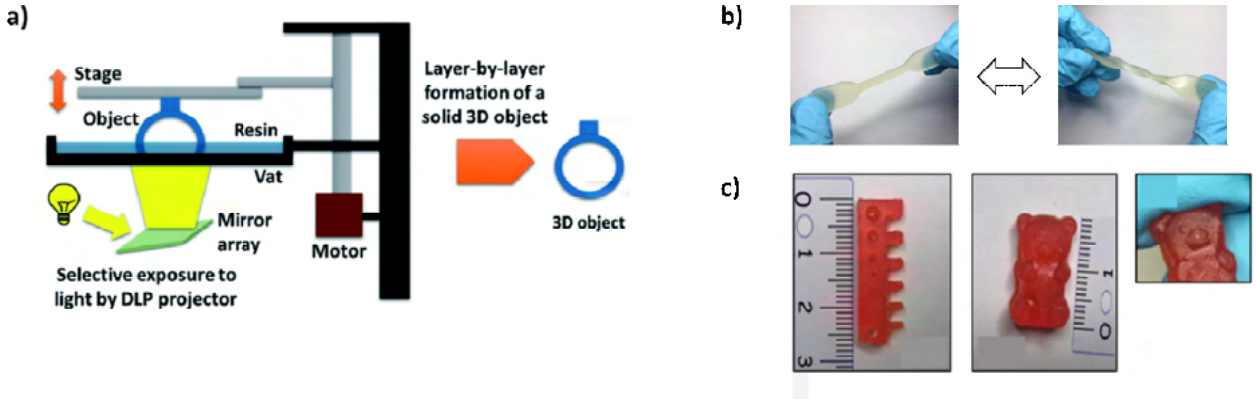

Figure: Schematic presentation of (a) the DLP 3D-printing process, (b) reversible twisting of the photo-cured rubber specimen and (c) DLP 3D-printed objects with precise structures.

For the DLP 3D-printing of liquid isoprene rubber, several challenges have to be faced. In general, the poor photo-reactivity of diene-rubbers makes them not applicablefor DLP printing. However, this can be overcome by either introducing photo-sensitive moieties such as (meth)acrylates in the sidechain of the rubber or by using thiol-click chemistry.[2] A further critical point is the high viscosity of the liquid rubbers, which limits their processability for DLP 3D-printing. To overcome this disadvantge, various divinylethers and thiols were used as reactive diluents. Upon the addition of reactive diluents not only the viscosity was adjusted to a processable level but also the photo-reactivity was increased significantly. This led to a successful DLP 3D-printing of liquid rubber specimen with a high precision.

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Association Dynamics of Supramolecular Polymer Blends

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In this work, we present a combined analysis of small angle neutron scattering (SANS), linear rheologyand neutron spin eco (NSE) spectroscopy experiments on thesupramolecular association and chain structure of supramolecular polymer blends. These consist of well-defined hydrogenated (H) polymers with a polyethylene oxide(PEO) backbone carrying the directed heterocomplementary hydrogen-bonding functional end-groups, thymine (thy)and diaminotriazine (dat), immersed in their own deuterated (D) covalent short linear non-functionalized PEO chains in the melt as solvent.The molar mass (M_W) of the functionalized (H) PEO is 2000 $gmol^{-1}$, and of the non-functionalized (D)PEO chains 500 $gmol^{-1}$. Their self-assembly and phase behavior in the melt state is investigated as a functionof temperature and supramolecular polymer mass fraction in the ideal blend.The melt structure is found to be well described by the Gaussian model [1,2], and the diffusion and viscositystudy revealed Rouse dynamics [1,2]. Based on a recently developed model approach to describe the dynamics of supramolecular polymers [3], NSE analysis directly revealed the hydrogen bond lifetime, but also that the debondingaffects the mode contribution rather than the relaxation times.

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Polyurethane/polyisocyanurate foams containing a physical bio-filler in the form of evening primrose (Oenotherabiennis) cakes

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Rigid polyurethane-polyisocyanurate (PUR/PIR) foams are among the best thermal insulation materials. The share of these materials in the total consumption of thermal insulation materials in the world is about 5%. The price of the finished product has a significant impact on this. Important components of the final price are the expensive and sometimes toxic products required to produce the foam. One of the methods of reducing the costs of polyurethane materials production is their physical modification. This modification consists in including powder or fibrous fillers into the technological formulation, which improve the desired properties, e.g. apparent density, compressive strength, brittleness or reduce flammability [1]. Environmental aspects are also an important element in the production of new materials. They concern the reduction of the negative impact of these materials on the environment (the possibility of biodegradation) and the replacement of petrochemical raw materials with e.g. plant-based counterparts [2].

Due to the growing problem of plastic waste management, many research centers are working on obtaining new, biodegradable polymeric materials. Such materials should demonstrate the functional properties of plastics obtained by conventional methods, and at the same time be recyclable, for example by composting. They are obtained on an industrial scale from both renewable and petrochemical raw materials. The use of oilseed cakes as fillers in the production of new polyurethane materials is innovative. The cakes are produced during the physical pressing of oilseeds. The significant increase in the amount of cake and meal in the country forces us to look for alternative methods of using them. Oilcakes can be used in animal nutrition as high-protein additives to plant fodder or as an ingredient for the production of silage. However, if the cake is not subjected to a sufficiently high temperature, it may contain anti-nutritional substances that have a negative impact on the health and productivity of animals [3]. The presented research describes the results of work on obtaining rigid polyurethane/polyisocyanurate foams containing a polyurethane matrix with an embedded filler fraction in the form of milled evening primrose cake.

Rigid polyurethane/polyisocyanurate foam formulations were modified by evening primrose (Oenotherabiennis) oil cake, as a bio-filler in the amount of 5 to 50 wt.%. The obtained foams were tested in terms of processing parameters, cellular structure (SEM analysis), physico-mechanical properties (apparent density, compressive strength, brittleness, accelerated aging tests), thermal insulation properties (thermal conductivity coefficient, closed cells content, absorbability and water absorption), flammability, smoke emission and thermal properties. The obtained test results showed that the amount of bio-filler had a significant influence on the morphology of the modified foams. Thorough mixing of the polyurethane premix allowed better homogenization of the bio-filler in the polyurethane matrix, resulting in a regular cellular structure. This resulted in an improvement in the physico-mechanical and thermal insulation properties, as well as a reduction of the flammability of the obtained materials. This research provided important information on the management of the waste product from the edible oil industry and the production process of fire-safe rigid PUR/PIR foams with improved performance properties.

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Intermolecular Information Transfer in Synthetic Macromolecules

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The study of sequence-defined polymers is a developing field of polymer chemistry, which is aiming for a precise control over macromolecular structure and, therefore, properties [1]. That could open some advantageous opportunities for material applications, as well as a better understanding of the mechanisms of Life, for instance regarding the essential concept of macromolecular information transfer [2]. While in Nature, information transfer is an efficient process optimized for billions of years, the idea to apply the same concept to artificial polymers is relatively recent [3]. Some inspiring examples of molecular recognition, template-directed synthesis and even self-replication of sequence-defined oligomers have been reported [4, 5]. However, synthesis of longer macromolecular chains that are structurally unrelated to nucleic acids and yet capable of information transfer remains challenging. Here, we describe information transfer from an oligourethane parent strand to a complementary daughter strand of different chemical nature using a covalent ester strategy (**Fig. 1**). The parent strand was synthesized by an iterative solid-state strategy previously optimized by our group [6]. Building blocks containing protected COOH- and OH- sidechains were used to construct this strand. The parent information sequence can then be potentially translated by (*i*) first selectively deprotecting the pendant groups, (*ii*) functionalizing the deprotected sites by esterification with polymerizable building blocks, (*iii*) polymerizing the daughter strand and (*iv*) releasing the daughter strand by hydrolysis.

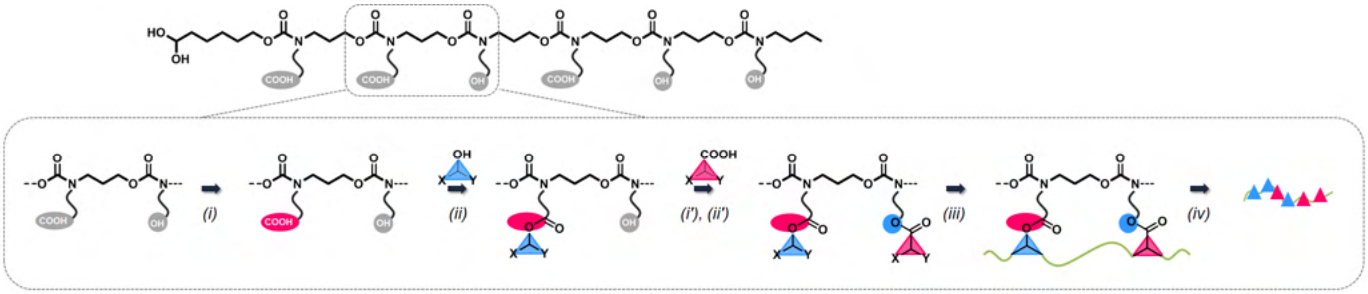

Fig. 1 Principle scheme of information transfer in a sequence-defined oligourethane: (*i*) deprotection of the pendant groups, (*ii*) esterification with polymerizable building blocks, (*iii*) polymerization and (*iv*) release of the daughter strand.

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Laterally-resolved molecular dynamics and charge transport properties of polymers by Atomic Force Microscopy

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The nanoscale investigation of polymers properties has become an increasingly attractive topic in the fields of device engineering and fundamental research. This interest is related to the possibility of obtaininga deep knowledge about polymer properties at the molecular level, able to serve as basis of the cutting-edge technology developments, such as functional nanostructured materials composed by heterogeneousphases.In this context, Atomic Force Microscopy (AFM) provides a powerful tool to study and understand polymer properties at broad length scales, ranging from micrometers down to single polymer chains, with the possibility of identifying phases with distinct responses (mechanical, electrical, chemical,…) [1]. In this sense, in recent years we have focused onto the development of an AFM-based technique able to provide information about the molecular dynamics and transport properties of polymers. This method, called nanoDielectric Spectroscopy (nDS),measures the electrical interaction between the AFM probe and the sample, in turn allowing to determine the frequency-dependent complex dielectric permittivity (ε*) of the material under investigation, with a lateral resolution up to a few tens of nanometers [2]. By nDS, it is possible to obtain dielectric maps showing phases with distinct dynamics, and local dielectric spectra that allow an in depth-study of molecular and charge relaxations [3]. Moreover, the nDS studies can be carried under controlled temperature and/or relative humidity conditions.

In this work, the study of nanostructured polymer thin films by nDS will be presented and discussed. First, a brief introduction to technique's fundamentals and advantages will be provided. Second, we will focus on providing two application examples:(1) The ionic transport properties of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) blends. In this case, we were able to monitor the ionic contribution to the dielectric response of the blends thin films in function of the fraction of the two components. (2)The study of the molecular dynamics of an all-polymer composite of poly(epichlorohydrin) (PECH) with PMMA-based single-chain polymer nanoparticles. Here, we observed how the surficial interaction between the two components can be addressed by nDS. To summarize the presentation, we will discuss possible correlations between nano- and macroscale studies, able to link the molecular level response with the resulting bulk material properties.

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Chemical Upcycling of PET waste to obtain high-added value products

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Nowadays, adopting a Circular Economy instead of a linear production procedure seems to be the ideal solution for the problematic Plastics waste treatment and management [1]. The recycling of Poly(ethylenterephthalate) (PET) can be part of this solution, as PET stand out for is excellent thermal and mechanical properties and its low production cost. The mechanical recycling of PET is well developed in the industry, but the procedure implies the loss of product properties compared with pristine PET; after the second cycle the properties decrease notably[2]. On the contrary, the chemical recycling presents versatile procedures and the possibility to obtain high value products. However, normally it requires drastic reaction conditions (high temperatures, pressures, etc.) that increases the production price and produces the loss of valuable product and finally its exclusion of the recycling cycle [2].

For those reasons, the aim of this project was the chemical recycling of PET in order to obtain polyols, under mild reaction conditions and with high versatility. Different basic catalysts and PET residues of different origin and pigmentation (monomer Bis(2-Hydroxyethyl) terephthalate (BHET) from PET glycolysis or grinded PET form different sources) were employed. In addition, the molecular weight and chemical composition of each resulting polyol was determined by ^{1}H-NMR using a procedure developed by our group [3]. The final objective of these polyols is to synthesize polyurethanes as a high value material.

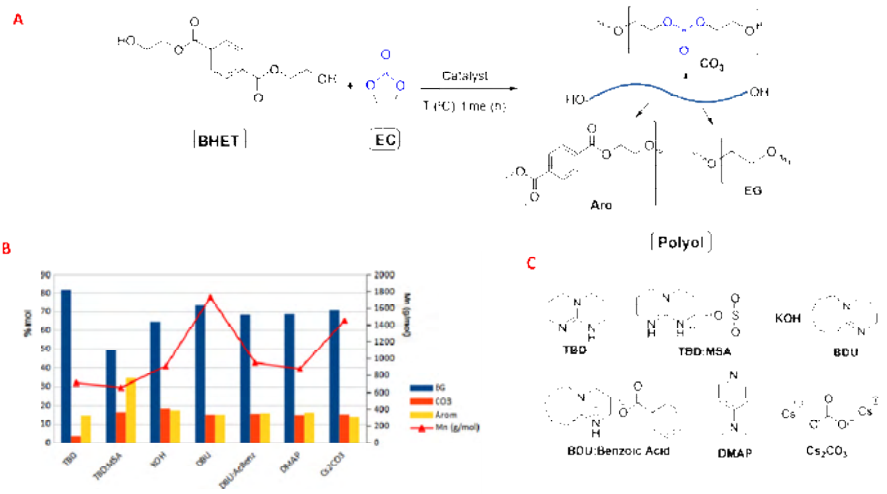

Figure 1: A) Synthetic scheme of the polyols from glycolized monomer BHET; B) Chemical composition and molecular weight of the polyol obtained by chemical recycled of BHET using different basic catalysts; C) Chemical structures of basic catalyst applied in the synthesis of polyols.

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Ethylene-1-octene elastomers: Molecular structure characterization by preparative fractionation and advanced analytical methods

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The market share of linear low density polyethylene (LLDPE) has continued to grow over the recent past due to its superior mechanical properties. LLDPE copolymers can be tailored to have different densities by simply altering the comonomer content/chemical composition (CC). Ethylene-1-octene (EO) copolymers with high 1-octene content are known as plastomer/polyolefin elastomers, and therefore lack crystallinity. Over the years, crystallization-based techniques have been developed that form the backbone of polyolefin characterization. These include differential scanning calorimetry (DSC), crystallization analysis fractionation (CRYSTAF), temperature rising elution fractionation (TREF) and more recently crystallization elution fractionation (CEF). However, these crystallization-based techniques are limited to semicrystalline material in their characterization, hence become redundant for molecular structure characterization of elastomers.

In the first part of this work four different preparative fractionation techniques including solution crystallization fractionation (p-SCF), temperature rising elution fraction (p-TREF), modified (p-TREF) and molar mass fraction (p-MMF) were evaluated for molecular structure characterization of EO elastomers. It was shown p-MMF is a suitable for preparative fractionation EO LLDPE elastomer, consequently, was employed in the second and third part of this for a comprehensive molecular structure characterization of four LLDPEs with varying 1-octene content (second part), and LLDPEs with specifically 1-octene content greater than 10 mol%. It was proven that p-MMF method in combination with FTIR, HT-SGIC and 2D-LC provides comprehensive molecular structural information of less crystalline EO LLDPE elastomers.

Study of multi-scale resin structuration and its impact on macroscopic properties in the resin filled elastomer blend system

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In this study a new type of elastomer systems, seen as an alternative for conventional nanocomposites widely used in industrial applications such as tire industry, was prepared and investigated thoroughly. They are made of an SBR (Styrene-Butadiene Rubber) matrix, blended with low molecular weight and high Tg resins. Such materials raise different questions: How does the resin incorporation influence the elastomer network structure? Depending on the miscibility and the resin content, what is the resulting morphology? How does the morphology evolve with the temperature, the processing condition and the crosslinking protocol? And of course, how this morphology impacts the macroscopic mechanical properties?

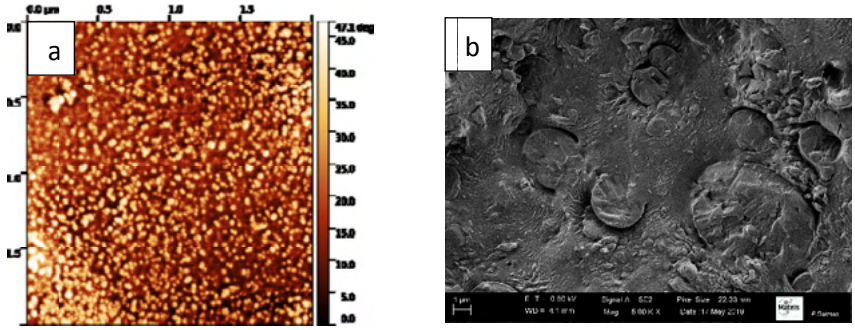

Figure: a) AFM phase image of blend with 25 wt% of resin, b) SEM image of blend with 45wt% of resin.

One of the studied resins is semi-compatible with the polymer matrix. A multi-scale phase separation (from nano to micrometer scale) was confirmed using DSC analysis, DMA experiments, scanning/transmission electron microscopy (SEM/TEM), atomic force microscopy (AFM) and small angle X-ray scattering analysis (SAXS). Nanocomposite-like morphology (nano-domains of size of 20-35 nm) was highlighted by AFM (figure 1a) in the blend and micro-domains whose number and size (1-5 μm) increase with the resin concentration were evidenced by TEM and SEM (Figure 1b). Swelling measurement showed that resin is fully extracted by the solvent, confirmed by the DMA and morphological analysis done on the samples after resin extraction, and thus does not significantly react with the matrix. Nevertheless, the presence of resin during the processing of materials leads to a decrease of the entanglement/crosslinking density of the network, explained by the swelling of the matrix by part of the resin prior to its crosslinking. This was confirmed by NMR. Rheological analysis done on uncured samples and slip tube model given by Rubinstein and Panyukov [1] applied on resin extracted samples confirm the dominance of entanglements over chemical cross-links. Volume fraction of rigid inclusions was quantitatively estimated using self-consistent modeling approach (C-L model)applied on the dynamic mechanical behavior of blend system [2]. However, the contribution of phase separatedrigid fraction on the macroscopic properties in the form of micro and nano-domains is not clear and under investigation. Ongoing work tries to decorrelate the distinguished contribution of nano and micro domains on the macroscopic mechanical properties and understand the thermal stability of nano-domains at short and long time, before and after thermal treatment.

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PET surfaces with hydrophobic properties

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The development of non-stick properties in polymeric surfaces is one of the most attractive tools to the growing need to adapt these materials to the objectives of the circular economy. The reinvention of plastics in the transition to circular economy [1] is an imperative due to their widespread use, but also because of the possibilities they offer as a material for adaptability in reuse, reprocess and recycling, which is not available to most conventional materials. In this sense, controlling wetting properties helps to optimize the use of resources and favor recyclability by adding otherproperties to surfaces,such as self-cleaning, antiicing or antimicrobial [2].

Non-wetting behaviour arising from superhydrophobicity is typically achieved by the generation of roughness at micrometric and even nanometric scales. To this purpose, expensive and poorly scalable methods, such as lithography, laser ablation orinorganic particles coatings have been traditionally used, not favoring recyclability and sustainability. Progress in this regard should be focused on achieving non-stick propertiesin an industrially viable method,avoiding both the use of inorganic particles (to facilitate recyclability) and the deposition of external coatings(to boost mechanical stability).

Based on the research group know-how [3]with other polymer surfaces, in this work, Polyethylene terephthalate (PET), one of the most widely used polymers specially in packaging industry, has been used as a starting material for the preparation of non-wetting surfaces. Non-stick properties are achieved through a fast, simple and scalable method. The generation of roughness for the appearance of hydrophobic properties has been sought by immersion in different solvents of amorphous PET films to induce crystallization. The possibility of using recycled PET (rPET) has also been explored since the new UE regulations oblige to add at least 25wt% rPETin packaging by 2025, and rPETinfluences the crystallization behavior.Solvent-induced crystallization has been widely explored and optimized to generate homogeneous roughness. Immersion in CH_2Cl_2 give rise to the best results with a post fluorinated treatment to improve hydrophobia.These as-treated surfaces were characterized by optical profilometry and SEM and their wetting behavior was studied by measuring the contact angles and hysteresis (Figure 1). Promising early results have been obtained with contact angles greater than 150 degrees.

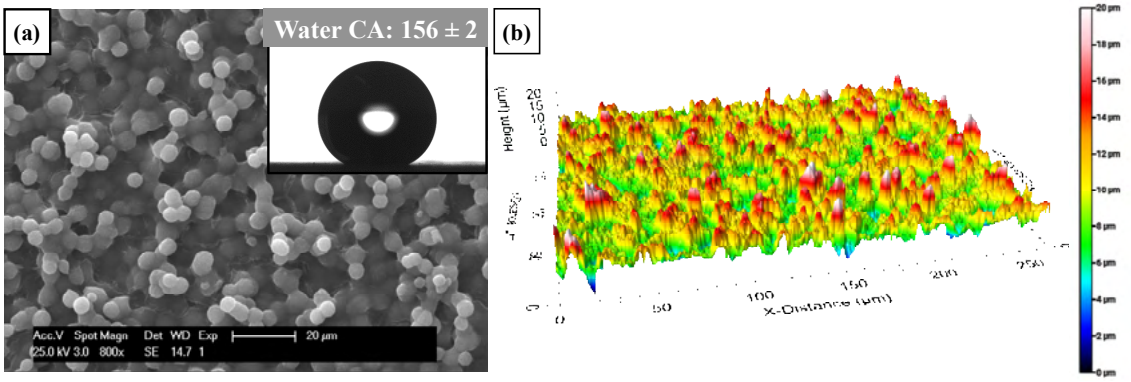

Figure 1:(a) SEM micrograph at 800x of PET rough surface and contact angle of water (b) 3D-optical profilometry imageat 50x.

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Removing heavy metal ions from water using PAA-based hydrogels

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Nowadays over 80 countries in which live about 40% of people, struggle with lack of water resources. In next few years the situation can be even worse due to overpopulation and climate changes[1].Current drinking water resources are being downsized by heavy metal contamination, which seeps through the rivers from sewages[2].Therefore, it is urgent to find new ways of water treatment.Currently common methods are filtration, ion exchange and precipitation[3].In our study, we would like to present a new method of water treatment using PAA hydrogel.

Hydrogel is a three-dimensional network of polymers created eitherusing covalent bonds or intramolecular interactions. Such system is full of pores which in case of hydrogels are filled with water molecules[4]. Thanks to such a structure a polymer obtains characteristics vitally varying from non-gel structure polymer chains. For instance, PAA based gels are insoluble in water while oligomeric and polymeric structures of acrylic acid are well-miscible with this vastly used solvent. Poly(acrylic acid)hydrogel structure ismuch more applicable in binding the metal cations than linear chain structure because of two reasons – first, the negatively charged carboxylate groups, despite beingless frequent (due to the presence of cross-linkers) are more densely packed than in long PAA chains, and secondly, there is a space in the gel pores to trap the ions inside comparing to no such space in linear structure.

In order to remove the aforementioned ions from water polymer hydrogels were synthesized. Acrylic acid (AA) was mixed with appropriate amounts of crosslinker, ethylene glycol dimethacrylate (EGDMA), water and then polymerized by ultraviolet light irradiation. Obtained hydrogels were then characterized. Swelling ratio of about 140% in clean water was obtained. Next the hydrogels were immersed in solutions containing heavy metal ions such as iron or copper, in order to determine their capacity and the concentration of ions left in water in the equilibrium state, which was measured using UV-Vis spectroscopy.Results show that vast majority of metal ions is absorbed by the polymer.

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Removal of hexavalent chromium ions bysponge-like polypyrrole–nanofibrillated cellulose aerogels

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Soft electronics are in high demand due to their wide range of applications.Conducting gels provide the electrical conductivity beside their high mechanical flexibility. Polypyrrole hasattracted more interestamong other conducting polymers due to itshigh electrical conductivity [1, 2]. One-step preparation of polypyrrole–nanofibrillated cellulose (PPy–NFC) cryogels were achieved by the in situ oxidative cryopolymerization of pyrrole in the presence of NFC (Fig. 1). A series of polymerization with various content of NFC (0.1 to 2 wt.%) was performedunder frozen condition.The corresponding sponge-like, lightweight, flexible and conducting aerogelswere producedby the freeze-drying of the cryogels. Entangled, three-dimensional and micro-/macro-porous networks with various pore sizes were obtained with high specific surface area (34.5–67.3 m^2/g). The cryogels mechanical properties were found to increase by increasing the NFC content. The maximum tensile modulus of 1055 kPa was achieved for the aerogel prepared with 2 wt.% of NFC. The electrical conductivity in the range of 19 to 31 S/cm was achieved in the case of protonated aerogels and 0.025 to 0.7 S/cm of the neutral aerogels. The aerogels revealed high affinity towards the hexavalent chromium ions with a maximum adsorption capacity of 183.6 mg/g in the case of PPy–NFC aerogel prepared with 0.3 wt.% of NFC. The high adsorption capacity of the aerogels is due to their high specific surface area and ion exchange properties.

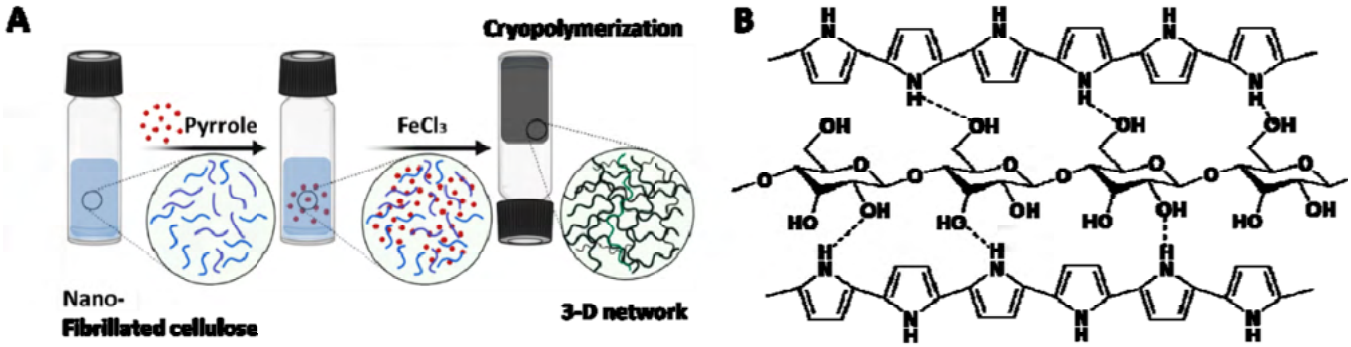

Fig. 1. (A)Schematic of cryogel formation, (B) proposed chemical structure of polypyrrole–nanofibrillated cellulose cryogel.

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Study of the adsorption of methylene blue by octenyl succinic anhydridefunctionalized starch

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Methylene blue (MB) is a serious hazard to our health and the environment and in small amounts can contaminate large amounts of water[1]. In the present work, a corn starch(S) and a potato starch (PS) were modified with Octenyl Succinic Anhydride (OSA),and their ability to remove MB was evaluated.We studied the influence of pH of the MB solution in a range of 3 to 9, adsorbent concentration (150 ppm, 300 ppm, and 450 ppm), and MB concentration (10 to 25 ppm). The characterization of the modified starches was done byFTIR, H^1NMR,TGA, DRX, and SEM. The adsorption of MB by S and PS in aqueous solutionsis also studied. The degree of substitution (DS) for corn starch modified with OSA (SOSA) was 0.0093 and 0.014 for modified potato starch (PSOSA). The removal percentage of MB by S and PS was 16.5±5.1 %, and 14.2±1.1 % respectively. For the modified starches, the removal percentages increased to 47.9±3.7 and 68.8±4.8 for the SOSA and PSOSA respectively. It is important to mention that the removal percentage and adsorption with PS is higher than with S. This could be attributed to the crystalline structure; the PS has a hexagonal structure and the S has a monoclinic structure. This implies that PS has more space for the transport of the contaminants and generates better adsorption, even in the modification the DS in PS is higher [2]. The best adsorption results were obtained at pH 9, on this pH value, there is an interaction between the alkoxide group of the modified starches and the cationic dye. The adsorption capacity depends on the electrostatic differences and the dipole-dipole interactions [3]. When the adsorbent concentration (PS) wasincreased, the removal percentage of MB was increased, for 150 ppm of PS the percentage was 41.5±3.1%, with 300 ppm was 62.5±5.6% and finally, with 450 ppm the percentage was 68.8±4.8, the higher concentration of absorbent implies more available sites for the adsorption[4].Furthermore, with an increase in the concentration of MB the kinetics constants become smaller, the kinetic studies have shown that with a higher concentration of MB the speed of the adsorption was lower, it was due to the fact that there is less space available in the adsorbent. The model that has followed is a pseudo second order indicating that the process that has followed the adsorption is chemisorption. On the other hand, the isotherm at a temperature of 25^{o}C follows the Freundlich model with a 1/n of 0.77 indicating that the adsorption is favorable and the surface of the adsorbent is heterogeneous. One of the conclusions of the experiment is that the best condition of adsorption with the PSOSA was at 450 ppm of adsorbent, with adsorption of 27.5 mg/g and 70% of removal in 60 min.

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Polysaccharide-based flocculants for filter backwash water treatment

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One of the highly effective methods of water treatment is flocculation. Itis the phenomenon of aggregates formation due to the adsorption of macromolecules of polymeric compounds on the surface of solid-phase particles, which accelerates their sedimentation.The substances used in this process are called flocculants, as the most commonly used synthetic polymers, such as polyacrylamide and its derivatives. However, their use is associated with problems such as non-biodegradability and the possibility of dispersion of toxic monomer residues in water, which can be a health hazard[1].

Therefore, scientists are looking for an effective method of replacing synthetic flocculants with natural organic polymers that are biodegradable and non-toxic, which minimizes their negative impact on the environment and is a part of the ecological methods of water purification.Polysaccharides, such as chitosan or starch, are of particular interest. The main advantage of this type of compound is its relatively wide availability, easy chemical modification, non-toxicity, and high efficiency in the aggregation of impurities. Based on these reports, it can be assumed that the practical use of bio-flocculants as innovative agents in water treatment will rapidlygrow [2].

Our research aimed to determine the efficiency of water purification at the Water Treatment Plant (WTP) in Kutno using new bioflocculants based on chitosan and modified starch. The tests investigated the effectiveness of removing iron compounds, the high concentration of which mainly determines the increased turbidity of the treated water. The results were compared with the previously conducted research on the flocculation process of filter backwash water at the WTP in Kutno using popular flocculants available on the Polish market [3]. With the help of biopolymers, over 90% reduction of the tested water parameters was achieved, corresponding to the values obtained for commercial flocculants. The results indicate the possibility of efficient replacement of synthetic polymers by flocculants based on biopolymers, such as chitosan and modified starch.

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Assessment of flammability of polyurethane/polyisocyanurate foams based on bio-polyol containing boron and sulfur atoms

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Polyurethanes are an important group of materials due to their wide application in everyday life. The use of these materials is directly related to their properties: physical (density), mechanical (brittleness, compressive strength), thermal (thermal conductivity coefficent) and, above all, flammability. Economic and environmental aspects, such as. impact on the natural environment, are also an important element. Often, the desire to obtain specific properties of polyurethanes is associated with the addition of auxiliary substances and flame retardants into the technological formulation [1, 2]. The current trends are aimed at obtaining ecological product solutions while maintaining the strategy of sustainable development [3].

The use of compounds containing boron and sulfur heteroatoms in conducted research for the preparation of polyurethane/polyisocyanurate foams based on them resulted in the improvement of fire resistance of this materials. Moreover, it contributed to the elimination of toxic halogen-based flame retardants, e.g. organic chlorophosphates.The presented research contributes to the reduction of the consumption of petrochemical raw materials resulting from the processing of crude oil in favor of easily renewable raw materials of plant origin. This also enables replacement of the toxic flame retardants in polyurethane foams with substances that do not have a negative impact on the environment.

The presented research shows the practical application of bio-polyol obtained on the basis of white mustard oil for the production of rigid polyurethane/polyisocyanurate foams. The influence of the synergism of boron and sulfur heteroatoms on the flammability of the obtained materials was also investigated. This was done by testing the obtained polyurethane materials with numerous flammability tests, including Bütler chimney test (according to ASTM D3014-04), horizontal burning test (according to PN-EN ISO 3582:2002/A1:2008), limited oxygen index (LOI, according to ISO 4589) and the cone calorimetry method (testing the fire and smoke generation properties of tested materials according to ISO 5660:2015).

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Novel phosphoramide-based monomers for flame retardant polymers

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Flame retardant materials are importantsubstances in our modern life. They can be used to delay the ignition time or limit the spread of the fire.However, although halogen-containing flame retardants are very effective, they have negative impact on the environment [1]. In contrast, phosphorus-containing polymers are less harmful. Therefore, the aim of our work is related to the synthesis of various monomers forobtaining flame retardant polymers with phosphorus moiety using ring-opening metathesis polymerization (ROMP). Sincenorbornene is easily polymerized by ROMP,our aim was to prepare P-containing norbornene with phosphorus-carbon bond (Figure 1).

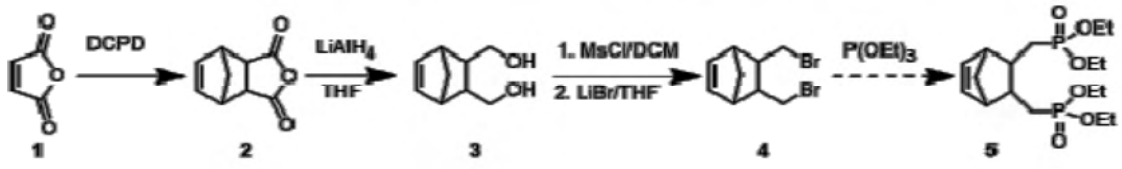

Figure 1: Planned reaction route to prepare monomer **5**.

The starting compound was maleic anhydride (**1**), an excellent substrate for Diels-Alder reactions. Norbornene-yl-anhydride (**2**) was formed by the Diels-Alder reaction of maleic anhydride (**1**) with in-situ generated cyclopentadiene from its dimer (DCPD) [1].The formed adduct **2**was reduced to diol (**3**) by $LiAlH_4$at 0°C in THF [2].Diol **3** was converted to the dibromide(**4**) by mesylation followed by bromination. The crude product was purified by column chromatography.The next step was the Arbuzov reaction of**4** to preparethe desired diphosphonate (**5**). This monomer waseffectively homopolymerized and copolymerized with norbornene to polynorbornene derivativesin the presence of ruthenium containingGrubb's catalysts. Further advantage of this compound is its phosphor-carbon bonds which increases the resistance against fire.

Figure 2: Synthesis of phosphoramide monomers **7** and **9** for ROMP.

Our second aim was to synthesize a monomer which contains phosphoramide moieties (**7**,**9**). Norbornene containing both primary amine (**6**) and secondary amine (**8**) were transformed to the desired flame retardant monomers which also act as crosslinkers in ROMP (Figure 2). The secondary amine **8** was prepared by the formation of an imine from 5-norbornene-2-methylamine and 5-norbornene-2-carboxaldehyde followed by a reduction using $NaBH_4$. The resulting crude product waspurified by column chromatography.The pure product was reacted with phosphorus oxychloride to achieve the desired triamide**9**. All the monomers prepared were characterized by NMR and LC-MS measurements.

The copolymerization of the triamide**7** and norbornene was carried out with different comonomer ratios, and the polymers were characterized by TG measurements.

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Synthesis of flame-retardant bio-polyol based on white mustard (*Sinapis alba*) seed oil containing boron and sulfur atoms

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The most popular methods of implementing the principle of sustainable development in the polyurethane materials industry is the use of components based on raw materials of natural origin (such as, bio-polyols or bio-fillers) for their production [1, 2]. This research presents the method of using unrefined white mustard (Sinapis alba) seed oil for the synthesis of a flame-retardant bio-polyol containing boron and sulfur heteroatoms dedicated to the preparation of rigid polyurethane/polyisocyanurate (PUR/PIR) foams.

The technology of bio-polyol synthesis consists in the chemical processing of oleochemical raw materials (such as vegetable oils) into polyhydric alcohols containing active hydroxyl groups capable of reacting, for example, with isocyanates [3]. In this research, white mustard oil was used as a basic raw material for synthesis of new bio-polyol. The use of this oil was not accidental because it contains a very high amount of unsaturated fatty acids (UFAs) in its composition. The content of UFAs in mustard oil is about 97-98% of all fatty acids and is the highest among oils available on the market. The high content of unsaturated fatty acids allows the use of this oleochemical raw material for the synthesis of various bio-polyols. It is possible to obtain products dedicated to rigid or flexible foams, as well as elastomers and other polyurethane materials by changing the qualitative and quantitative composition of reaction system. The main difference is the range of obtained hydroxyl numbers, which determine the potential applications of the obtained bio-polyols. Research on the synthesis of flame retardant bio-polyol based on white mustard oil is extremely important for the principles of sustainable development, which are the driving force of many companies in the European Union, especially in the chemical sector. These studies are also consistent with the principles of Green Chemistry, which strive to eliminate harmful, toxic and dangerous raw materials from production processes in favor of environmentally friendly raw materials, as well as human health and life.

Bio-polyol based on white mustard oil was obtained in a three-stage synthesis. The first stage was the epoxidation reaction of the double bonds in the plant raw material by *in situ* generated peracetic acid. The second stage of synthesis was the esterification reaction of boric acid with thiodiethylene glycol. The esterification reaction was carried out by azeotropic distillation, as a result of which the low molecular weight product (water) formed in the reaction was removed. The obtained boric acid ester of thiodiglycol was used for the third stage of the synthesis, which was the opening of oxirane rings of the epoxidized oil. This led to obtain the assumed bio-polyol.

The obtained bio-polyol was subjected to physicochemical tests such as: determination of iodine value, epoxyvalue, hydroxyl number, acid number, pH, density, viscosity and water content. Its average molecular weightand elemental composition were also tested. The presence of characteristic functional groups and assumed chemical structure were confirmed by spectroscopic methods (FTIR, ^{1}H NMR and ^{13}C NMR).

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Sustainable Approach to Fabricate Epoxy/ Nanocellulose Composites and Their Properties

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The future for polymeric materials has become uncertain as a consequence of environmental problems and also due to the decline of petroleum reserves. The need for performant thermoset materials led to the development of new ecofriendly materials from renewable resources, which proved to be a promising solution to fulfill the demand of sustainable development [1].

Vegetable oils (VO) represent a strong alternative for the conventional petroleum-based chemicals representing a viable strategy, due to their nature, versatile structure, low price and availability [2]. The epoxidation of different VO generates in the last decade new research strategies and thus, new epoxy matrices with superior performances were fabricated through different processes [3].Due to their long aliphatic chains (C18), VO-based polymeric materials are not enough mechanical strength, but these shortcomings can be easily mitigated by using different strategies of reinforcement.

Cellulose is one of the most abundant natural polymers, and it has been used as a raw material in the production of fibers and derivatives that have a wide range of applicability.Besides inherent renewability and biodegradability, the cellulose nanocrystals show great potential in bio-nanocomposites fabrication as reinforcing agent generating superior mechanical properties but not only [4].

Considering these aspects, our strategy was focusedon the development of new bio-basednanocomposites, starting from epoxidized linseed oil (ELO)loaded with different nanocellulose amounts (NC, extracted from plum seed). To fabricate the new ELO-NC composites materials with the aid of a sustainable strategy, citric acid was employed as non-toxic crosslinking agent.

Differential scanning calorimetry (DSC) and Fourier transform infrared spectrometry (FTIR) were used to monitor the thermal curing reactions, both techniques being employed to confirm the network formation and to define the curing kinetics. The effect of different NC concentration on the polymeric matrix derived from VO-based epoxy resin was studied, considering thermal and mechanical behavior, water affinity and biodegradability.

Acknowledgement: Authors acknowledge Ministry of National Education for funding through project no. 530PED/ 2020 (EPOCEL).

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Anisotropic epoxy composites with TiO_2 nanorods

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The investigation of an anisotropic epoxy composite was carried out. The composite consists of liquid crystalline epoxy resin MU22, the amine hardener *m*-PDA and TiO_2 nanorods. The matrix MU22/*m*-PDA was also prepared. The curing conditions were established on the basis of previous researches [1]. Curing proceeded in the presence of magnetic field with an induction of 1,2 T and without presence of this field. It was a factor that significantly influenced the ordering of mesogens in the nanocomposite, which is supported by other studies [2]. Degree of order and morphological properties were examined through DSC and WAXS analyses. The obtained DSC thermograms and WAXS diffractograms were analyzed. The results allowed to establish that the MU22/*m*-PDA composition cured at 180°C for 180 min is fully cured, while maintaining the oriented nematic structure. Samples of the MU22/*m*-PDA/TiO_2 composition require a cure temperature greater than 170°C and less than 190°C to obtain a crosslinked and ordered also nematic liquid crystalline structure.

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Pyrethroid insecticidal interior decorative coatings – an HPLC study to understand residual efficacy

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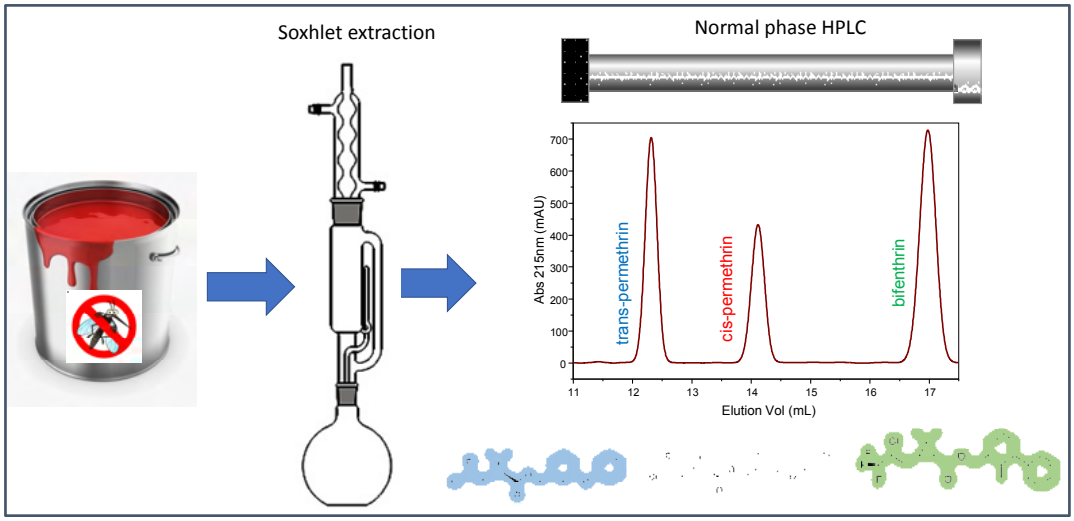
Mosquitoes known to be malaria vectors continue to affect many regions in Africa. To mitigate the detrimental health effects arising from the cohabitation of such species with humans, pyrethroid-based interior decorative coatings are being developed [1, 2]. The paints are seen as a viable option to improve the longevity of the insecticides. However, before the insecticidal paints can find widespread application, there is need to develop analytical methods to quantify the levels of pyrethroid insecticides in the paint. The analytical information is important to determine the quality of the product and the safety profile of the insecticidal paint to humans and the environment.

In this work, a systematic study of methods for the extraction of pyrethroids from complex paint matrices was carried out. A selective normal phase HPLC method was developed and then used to identify the analytes based on the elution of the analytical standards. Matrix-matched multi-points external calibration lines were constructed based on the peak areas of eluting standards from which the quantity of pyrethroids (trans-permethrin, cis-permethrin and bifenthrin) in paint samples were extrapolated. The results collected from the aforesaid procedures accurately and precisely confirmed the declared quantity of pyrethroids in the paint formulation. Furthermore, the residual pyrethroid content was shown to be significant for a couple of years after application of the paints- a remarkable outcome for product safety and quality.



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Poster Session II

Monday, September 27th

Polymeric capsules templated on liquid cores as nanoreactors

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Investigation of the processes taking place in attoliter volume (10^{-18} L) systems is crucial for many disciplines, such as molecular biology and advanced synthetic chemistry. Producing micro- and nanoreactors allows to carry out efficient and selective chemical reactions [1]. Polymeric micro- and nanosystems are efficient containers of hydrophobic and lipophilic substrates and can be formed by self-assembling hydrophobically modified polymers in aqueous media. These polymers provide unique core-shell structure wherein the liquid core serves as carrier for hydrophobic substrats and the ionic hydrophilic shell stabilizes particles in aqueous solution without any surfactants [2].

In this work we present model capsules as micro- and nanoreactors. Amphiphilic polyelectrolytes with comb-like graft architecture were used for formation of nanocapsules. Different polyelectrolytes were obtained and characterized in order to optimize properties of nanocapsules towards enhancing the ability for encapsulation of hydrophobic compounds. Physicochemical properties and stability of obtained polymeric capsules were investigated by dynamic light scattering, zeta potential measurements, scanning electron microscopy imaging and nanoparticle tracking analysis. The ability to encapsulate hydrophobic compounds was confirmed by confocal microscopy.

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Application of stilbene derivatives as photosensitizers of idonium salt for monitoring of various photopolymerization processe

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Currently, photopolymerization processes are used in many industries and also in medicine due to a number of advantages that they have. The production of polymeric materials using this method is developing rapidly and is widespread. The advantages of photochemical processes are low energy consumption, high speed and environmental friendliness. Moreover, these processes can be carried out at room temperature. Application of photopolymerization processes is mainly in production of photocurable varnishes and polymer coatings. However, currently photopolymerization is also widely used in medicine, dentistry and tissue engineering. A different direction of application of light-initiated processes is their use for 3D printing[1].

Nowadays a very important aspect is the search for compounds that are able to act as photosensitizers.The reason for this is that current light sources in the form of UV-LEDs and VIS-LEDs emit radiation that exceeds the absorption range of commercially used initiators such as diaryliodonium salts[2].

Applicability of stilbene derivatives as photosensitizers of idonium salt for monitoring of cationic photopolymerization of epoxy and glycidyl monomers and free-radical photopolymerization of acrylate monomer by FT-IR real time has been studied.

Based on researches new compounds can be used for monitoring fast photopolimeryzationproccess. These compounds are suitable for monitoring the kinetics of cationic and free-radical photopolymerization. Compounds can also be used as sensitizers in bimolecular initiator systems

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Amphiphilic and Double-Hydrophilic Block Copolymers with a Strong Anionic Segment from Low ppm Cu(0)-Mediated 'Living' Radical Polymerisation

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Block copolymers featuring both hydrophobic and ionic segments are highly valuable, due to their strong amphiphilicity and their ability to take part in electrostatic interactions. Often, these copolymers are based on weak polyelectrolytes, *i.e.* polymer segments with a pH-dependent charge density, which strongly restricts their useto anarrow pH window. While strong cationic segments can easily be achieved through mild and quasi-quantitative amine quaternisation [1], the efficient production of strong anionic polymers remains challenging. Direct polymerisation of negatively-charged monomers limits the possibilities for copolymerisation or chain-extension, while post-polymerisation modification of hydrophobic chains (*e.g.* sulphonation of polystyrene [2]) relies on harsh conditions that may not only affect the macromolecules end-groups but also any co-monomer present in the build. We have recently reported an efficient and facile route to produce strong anionic polymers in mild conditions [3]. This method usessturdy reversible addition-fragmentation chain-transfer polymerisation to produce hydrophobic isobutyl-protected sulphonate homo- and block copolymers and a nucleophile salt for the quantitative deprotection in DMSO at 70 °C.

Recently, another polymerisation technique, namely Cu(0)-mediated 'living' radical polymerisation (Cu(0)-LRP), has gained tremendous attention. Introduced in 2002 [4], itpicked up steamthanks to its ability to rapidly produce macromolecules at room temperature, achieve quasi-nominal conversion and use low amounts of catalyst without compromising the chains dispersity. Specialty monomers and in particular sulphonyl-containing ones are however notoriously prone to incompatibility or poor control in copper-catalysed polymerisation techniques and may require the use of complex solvent systems [5] or stabilising agents [6].

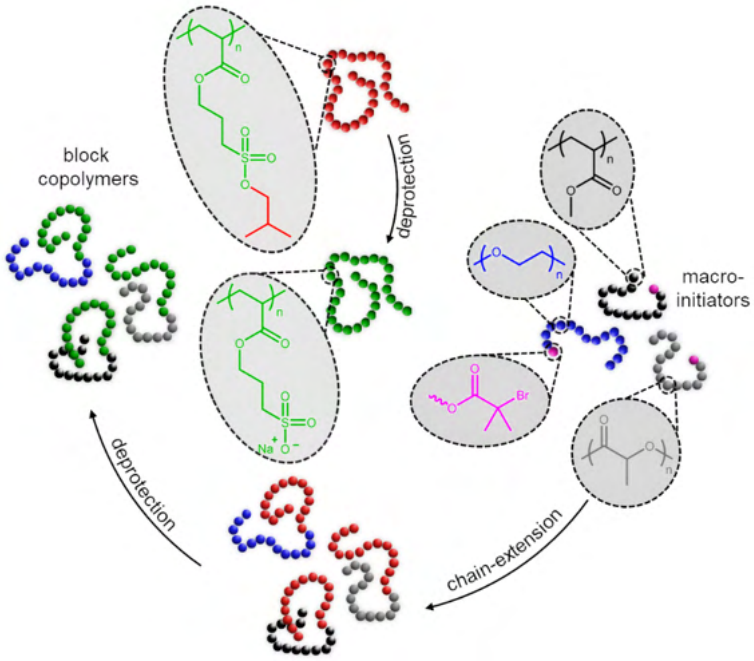

Figure 1: Schematic representation of the synthesis of sulphonyl-containing block copolymers

Herein, we explore the use of Cu(0)-LRP for the synthesis of isobutyl-protected sulphonate homopolymers and its deprotected counterpart, as well as a number of amphiphilic and double-hydrophilic block copolymers from the Cu(0)-LRP of functional macroinitiators.

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Compartmentalization of multi-enzymatic reactions in microfluidic devices and integration of polymersomes for additional reaction control

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Enzymesare characterized as valuable and powerful biocatalysts for chemical conversions of complex substrates under mild reaction conditions.Theirtriving usage for straightforward synthesis of (fine) chemicals, for final applications in food industries, production of pharmaceuticalsor realizing elegant biosensing concepts,rely on efficient strategies to avoid cross-inhibition and incompatible steps[1].
In addition,the requirementof different near-natural conditions of the respective enzymes for optimal activity often hinder the performance of such multi-step reactions in a one-pot approach and require labor-intensive step-by-step processes[2].

Therefor implementation and compartmentalization in microfluidic systems is a promising strategyto overcome these limitations and realizing serial and parallel multi-step reactions. We introduced PDMS-based microfluidic devices with multiple reaction compartments and enzymes immobilized therein. In this approach, a substrate solution is pumped through the device, stepwise converted upon contact with the enzymes and the corresponding product is continuously provided. Due to the spatial separation of the enzymes, cross-inhibitions can be circumvented and the reaction conditions can be tuned according to the need of the respective reaction steps. In detail, we investigated the entrapment of enzymes in hydrogel matrices and polymersomes as additional tool for increasing the complexity [3,4].

These are polymeric vesicles which were i.a. applied for the encapsulation of enzymes and introduced as nanoreactors. Thereby, stimuli-responsive polymersome membranes are able to turn the nanoreactor “on” and “off” by enabling or restricting the substrate diffusion towards the enzyme. Consequently, the integration of polymersomes into the microfluidic system is a valuable addition for achieving precise reaction control and compartmentalization of multi-step processes [5].

Currently we applied an enzymatic cascade using the classic model enzymes *Glucose Oxidase* (GOx) and in pH-responsive polymersomes entrapped *Horseradish Peroxidase* (HRP), separated on different type of hydrogel dots in a two-chamber microfluidic chip structure for optimizing the overall system and examining the limitations and challenges.

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Green solvents as a new tool for olefin metathesis polymerization and related reactions

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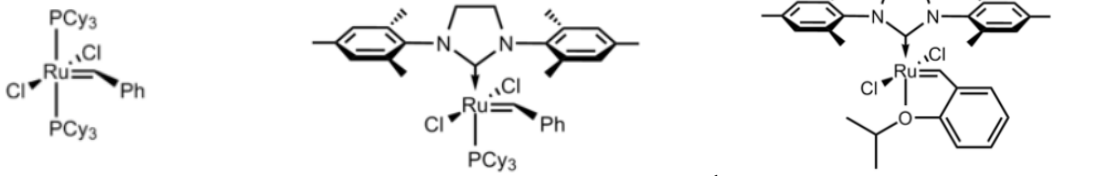
Olefin metathesis plays an important role in the field of pharmaceuticals, materials and petroleum refining processes. Olefin metathesis is a green process which involves a pair of carbon-carbon double bonds to be rearranged in order to form new products which can be more valuable compared to the starting ones. Due to its success in large scale industries [1,2], scientists tried to use more greener solvents to decrease the environmental impacts of this transformation process [3-5]. In this work, we have studied the effect of more green(er) solvents than dichloromethane (toxic solvent) on ring-opening metathesis polymerisation (ROMP, Scheme 1) with three commonly used ruthenium based catalysts in olefin metathesis (Figure 1).



1st generation Grubbs catalyst 2nd generation Grubbs catalyst 2nd generation Hoveyda-Grubbs catalyst

Figure 1. The structure of Grubbs catalysts used for the targeted reactions.

After our successful results, we have performed two more well-known metathesis reaction as ring-closing metathesis (RCM) and isomerization (Figure 2) using the same solvents and catalysts as in ROMP reactions. To compare the conditions and catalysts, kinetic measurements have been carried out for all the reactions using ^{1}H NMR. Besides, the polymers obtained by ROMP were characterized by gel permeation chromatography (GPC).

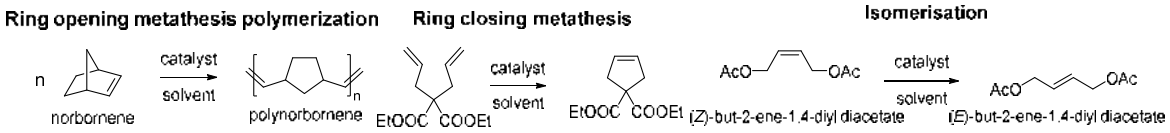


Figure 2. Different types of olefin metathesis reactions used in this project.

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Photopolymerization of cationic and free-radical monomers visible light using new chromophore based on a dihydrothiazolo[3,2-a]pyridineskeleton

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Photoinduced polymerization of monomers is gaining popularity as an environmentally friendly and safe method for production of protective polymer coatings on various surfaces. It has very advantages. The basic advantage of the photopolymerization over other methods used for preparation of polymer coatings is its speed. Photocurable compositions are transformed from a liquid state into a fully crosslinked solid within seconds or even fractions of second without emission of any volatile solvents to atmosphere. In addition to its high speed, the radiation curing provides several other advantages, in particular: ambient temperature operation, solvent free formulations, and low energy consumption [1].

Currently cationic photoinitiators can be used only in a limited part of the ultraviolet light usually range from UV-C to UV-B, bypassing the UV-A range and the visible range. Therefore, it is usually necessary to use co-initiators that guarantee the photochemical sensitivity of the initiating system and shift the emission spectrum into longer wavelengths[2]. In this work we present new compounds based on based on a dihydrothiazolo[3,2-a]pyridinechromophore which can be used as co-initiators for the cationic and radical photopolymerization processes. The research included the basic spectroscopic measurements, including, the measurement of emission and excitation spectra, fluorescence quenching after adding the diaryliodonium salt, photolysis measurements and monitoring of kinetic photopolymerization materials using Real-Time-FT-IR and photo-Differential Scanning Calorimetr tests.

In addition, the new compounds are also suitable as molecular sensors for monitoring and quality control of cationic, radical and thiol-photopolymerization processes using modern Fluorescence Probe Technology (in short FPT). In the FPT method, changes of fluorescence characteristics of appropriate molecular sensors, caused by changes of polarity, microviscosity or of the medium where the probe is dissolved, are monitored in real time. The FPT method is a non-destructive, which is well adaptable for monitoring very rapid processes, both on-line (i.e., where the sample moves in front of a detector), and off-line (i.e., in a quality control laboratory) [3].

Acknowledgments: This work was supported by the Foundation for Polish Science within the project TEM-TECH (project no. TEAM TECH/2016-2/15). Additional, special thanks to the project manager – dr hab. inż. Joanna Ortyl.

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Introduction of tetraphenylethane units to polylactide structure, resulting in obtaining new materials based on PLA

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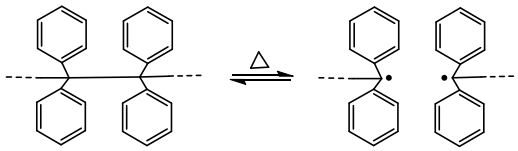
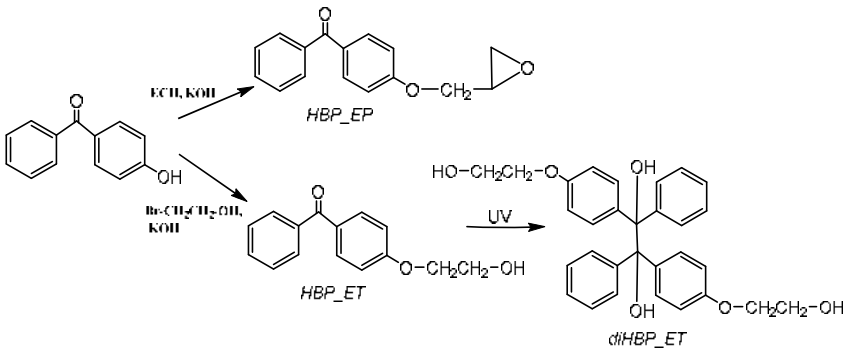
Tetraphenylethane(TPE) unit has been used as an „iniferter" in the polymerization of unsaturated monomers. The ability to its homolytic cleavage and to initiate a radical polymerization comes from relatively low energy of C-C bond when carbon atoms are substituted with four phenyl groups [1, 2] (Sch.1).



Scheme 1

Preliminary attempts to introduce TPE unitsinto PLA chain using tetreaphenylethenediol (TPED) to initiate lactide polimerization, and attempts of coupling TPE-diolwith PLA-diol using diisocynates turned out to be unefective, as a result of low reactivity of tertiary hydroxyl groups of TPED and side reactions of pinacol unit, which can accur in acidic or alkaline environment.

We developed new methods of chemical transformations, which let us obtain compounds that lead to TPE, and finally to polylactide with incorporated TPE units. These methods are based on using 4-hydroxybenzophenone as a starting point, its functionalization with specific groups and coupling to its derivative under UV radiation (Sch. 2). Corresponding units are being introduced to polymer chain through initating LA polymerization, or copolymerization with synthetized monomer, or by coupling with PLA-diol using diisocynate.



Scheme 2

Synthetized polymers basad on PLA will be used as „macroiniferters" to initiate polymerization of acrylates and to obtain products that are reversibly cross-linked.

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Quaternary ammonium urethane-dimethacrylate analogues – synthesis and characterization

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Dental composite restorative materials based on dimethacrylates are the most commonly used. This is mainly due to their mechanical properties, which significantly exceed those of other materials used in restorative dentistry [1]. Nevertheless, they are not perfect. Due to the high polymerization shrinkage, as well as due to the lack of antibacterial activity, inflammations and the formation of secondary caries are frequent phenomena associated with dental restorations performed with their use [2, 3].

The aim of this study was to synthesize and characterize six novel urethane-dimethacrylate derivatives (QAUDMA) containing two quaternary ammonium groups substituted with alkyl chain of various lengths. They consisted of two methacrylate groups, two urethane bonds, and 2,4,4-trimethylhexamethylene diisocyanate (TMDI) core. Due to such features of the chemical structure, they can be considered as analogues of the popular dental monomer, the so-called urethane-dimethacrylate monomer (UDMA). The design of noveldimethacrylate monomers containing quaternary ammonium groups aligns with the modern trends in the technology of dental materials, which stems from the need to develop bactericidal materials about satisfactory mechanical characteristics.

In the first part of this study, QAUDMAs were obtained by three-step process:i) transesterification of methyl methacrylate with N-methyldiethanolamine, ii) N-alkylation of the tertiary amino group with six various alkyl bromides, having from 8 to 18 carbon atoms, and iii) addition of TMDI to the intermediates achieved in the second stage. The chemical structure of intermediates and QAUDMAs were confirmed by Nuclear Magnetic Resonance spectroscopy (^{1}H and ^{13}C NMR). QAUDMAs were characterized in terms of their physicochemical properties and then polymerized. The obtained homopolymers (poly(QAUDMA)) were in turn tested in terms of their polymerization shrinkage and the degree of double bond conversion. The latter, was investigated by Fourier Transform Infrared Spectroscopy (FT IR) and Differential Scanning Calorimetry (DSC).

Obtained QAUDMAs were pale-straw colored resins, characterized by the refractive index values typical of dimethacrylates used in dentistry andviscosities over 1000-times higher than the viscosity of Bis-GMA. Their densities were mostly greater than those of commercial dimethacrylates. Their glass transition temperatures were lower than that of Bis-GMA, but higher than those of UDMA and TEGDMA. Polymerization shrinkages of poly(QAUDMAs) were comparable with polymerization shrinkage of Bis-GMA. The degrees of double bond conversion of poly(QAUDMAs), that were determined by FT IR and DSC analyses were similar and for each monomer significantly exceeded 50% (they ranged from 53 to 78%).

To conclude, obtained results confirmed that all six QAUDMA monomers can be used as components of matrices of dental composite restorative materials. As they meet the requirements for physicochemical properties of dental monomers, they will be subjected to further research towards the development of novel dental composite restorative materials with a capacity to reduce secondary caries and post-reconstructive inflammations.

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Dynamic covalent systems from formylphenylboronic acid derivatives

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The interest in dynamic covalent molecular systems has arisen as they are a convenient way to generate reprocessable and self-healing materials due to the reversible nature their crosslinks. Some examples of the interactions responsible for this behavior are disulfide bond formation [1], the Diels Alder reaction [2] or the boronic ester formation [3]. In the case of boronic acids, formylphenylboronic acids show a rich variety of interactions in addition to the formation of boronic ester, as they are also able of producing stable imines, oximes and hydrazones under the effect of the boron atom's empty orbital, even in aqueous media. These interactions can be seen Figure 1, including the special case of reactivity with acyl hydrazides, which leads to the formation of the boron-containing heterocycle diazaborine (DA).

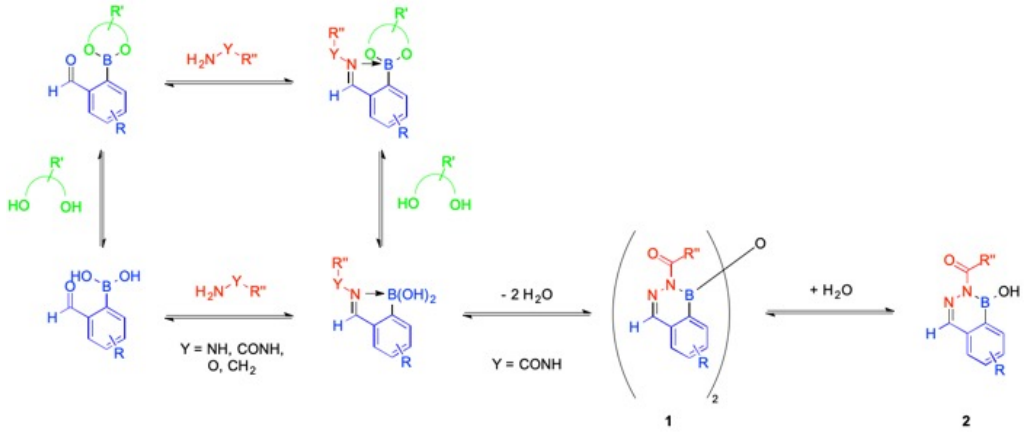

Figure 1. Reactions of interest between formylphenylboronic acid, nucleophiles and diol species.

The functionalization of water soluble polymers with formylphenylboronic acid moieties and the reaction with amine, hydroxylamine and hydrazide counterpartsmay lead to the development of macromolecular therapeutics and stimuli-responsive materials. In this work, several low molecular weight model systems have been prepared and characterized. The thermodynamic and kinetic properties of the dynamic interactions associated with Figure 1 have been studied by nuclear magnetic resonance (NMR) and isothermal titration calorimetry (ITC). In order to obtain appropriate materials for this study, several strategies have been designed to attach these functional groups to a series of polymeric scaffolds, leading to dynamic crosslinked systems.

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Supramolecular peptide/polymer hydrogels asself-healing biomaterials

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Peptide and polymer hydrogels are receiving increasing attention as substrates for cell growth and tissue engineering. Despite their many positive properties, covalently crosslinked polymer hydrogels lack biological functionality which can be overcome by employing supramolecular peptide hydrogels with a sequenced-defined chemical structure [1].Among them, Fmoc-FFpY has been selected due to their water solubility to be mixed with other aqueous solutions to form biocompatible hydrogels [2, 3]. Fmoc-FFpY can be self-assembled by electrostatic interaction in contact with cationic polymers, such as poly(allylamine hydrochloride) (PAH) [4, 5], leading to the formation of supramolecular hydrogels. Here, we present a new approach to develop hybrid hydrogels by electrostatic interaction of Fmoc-FFpY with cationic polymer nanoparticles (NPs),based on vinylimidazole and ketoprofen (poly(HKT-co-VI)), a non-steroidal anti-inflammatory drug that inhibits the inflammatory marker expression up to basal values. The electrostatic interactionyields a fibrillar gel network as observed by Cryogenic Transmission Electron Microscopy (Cryo-TEM). Rheological measurements proved the shear thinning behavior of the resulting hydrogels and self-healing properties to be used as injectable biomaterials. In vitro biological tests performed with human dermal fibroblasts (HDF) and RAW264.7 murine macrophages (RAW) cells showed the hydrogels biocompatibility, as well as their anti-inflammatory response. Overall, the supramolecular peptide/polymer nanoparticles based hydrogels show excellent chemical, mechanical and biological properties to be used as injectable hydrogels for tissue engineering applications [6].

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Rheological and Mechanical Behavior of Self-Healing Polydimethylsiloxane, Polyborosiloxane – Carbon Black Composites

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Nowadays, electronic devices are ineradicably integrated into our everyday life. However, many of them endure a failure due to mechanical stress and can not be repaired without parts replacing, contributing to the E-waste problem. Inspired by the tissue recovery capacity of living organisms after injuries, self-healing polymer-carbon composites are considered to be promising for flexible electronic devices to resolve the issue of their degradation and breakage [1]. In particular, polyborosiloxanes (PBS) provide fast healing properties due to dative boroxine bonding and supramolecular structure formed by hydrogen and coordinate covalent bonding [2].Moreover, the polymer possesses a large linear elastic region that demonstrates elastomer properties, making it very useful as a polymer matrix material. Recent studies considered various carbon materials such as graphene, graphene oxide, and multiwalled carbon nanotubes as conductive fillers for PBS matrix. However, most of the research misses discussion about the limits of applicability of such materials, providing insufficient data of their performance under different conditions.

Here we report the meticulous investigation of the rheological/mechanical behavior of composites based on carbon black as conductive filler and PDMS – PBS polymers with different relaxation times as matrices.We show that with filler tending to agglomerate, the electrical resistance is not constant but increases with time up to 100 times depending on polymer type, limiting the workability of such material for quantitative sensing purposes. In addition, we discuss the microstructure of the composites through electrochemical impedance spectroscopy analysis. The dynamic and relaxation tests reveal that in addition to polymer relaxation, carbon network relaxation occurs. Moreover, we demonstrate the difference in mechanical properties of such composites at shear strain applying at force exposure time lower and higher than the relaxation time of the polymer, where material may behave as plastic and elastic material, respectively. In addition, the rotational test shows that at a shear rate higher than polymer relaxation time, a material undergoes destruction and can not be spread or deformed with corresponding critical breakdown force. This study allows comprehending the carbon particles – polymer interaction and electromechanical characteristics of the composites to make a better material choice for a future flexible electronic device.

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Self-healable hydrogel platforms consisting of unimolecular micelles for enhanced drug solubility

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Modern nanomedicine aims to develop new drug formulations in order to increase the solubility of APIs (active pharmaceutical ingredients), which would in turn decrease the dose necessary and enhance the therapeutic benefits with lowered toxicity [1]. Up to date, many new formulations consider polymeric surfactant molecules and their ability to self-assemble into micelles. However, the drop below the CMC (critical micelle concentration) disrupts the architecture. Another approach for API solubilization is the utilization of amphiphilic block copolymers forming unimolecular micelles. Those constructs are independent from concentration and therefore more stable than polymeric micelles.

Vulvovaginitis is one of the most common gynaecological diseases worldwide [2]. The treatment usually involves vaginal suppositories. This treatment,however, suffers from poor adhesive properties and short retention time of water-insoluble drugs, such as nifuratel. Polymeric platforms seem to be a good candidate to improve the treatment against vaginal infections. The properties of polymers allow for the increase in the solubility of the drugs and more controlled release [3]. Moreover, hydrogels constructed of reversible cross-links are able to adjust the shape to the covered surface, and thus to form continuous coverage of infected areas prolonging the retention time of the pharmacological formulation [4].

The presentation adresses the challenge of the development of improved drug-solubility platforms. For the enhancement of water-insoluble drug nifuratel, we managed to synthesize the star-shaped unimolecular micelles by the anionic ring-opening copolymerization of furfuryl glycidyl ether and(1,2-isopropylidene glyceryl) glycidyl ether. The deprotection of the latter gave the hydrophilic 1,2-diols in the shell. The monomers were chosen carefully regarding their molecular structure. The furan containing side groups of the hydrophobic chains were thought to improve the solubility of nifuratel, which also contains the furan moiety in its structure. The 1,2-diol entities in hydrophilic poly(glyceryl glycerol ether) chain ensured the solubility of the construct in water. Furthermore, it allowed for the formation of boronic esters from boronic acids and1,2-diols. The cross-linking process assured the self-healing properties of prepared nifuratel-loaded hydrogel platforms.

The micelles exhibited high nifuratel loading capacity, the diffusion-controlled release mechanism revealed in *in vitro* release studies. The micelles showed no cytotoxicity towards human cervical cancer endothelial (HeLa) cells. Moreover, it has been noticed that the gel flows under applied stress and can therefore be delivered by a syringe to the afflicted area. The presented system shows great potential and will be further investigated.

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Cellulose acetate films and fibers produced using solution blow spinning- influence of solvent system

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Renewable, biodegradable polymers are recently receiving great attention because of their potential use in food packaging. Among the different variables affecting those materials, the way of preparation is a factor of primary importance, for example, in terms of the final morphology, dispersion of fillers if specific activity is required, etc. Solution blow spinning (SBS), a novel technique for nanofibers production, has been in usefor over a decade[1], being expandednowadays mainly in the preparation of polymer-based systems. Fibers and films have been prepared using SBS frompoly(methyl methacrylate) PMMA, poly(lactic acid) PLA, polystyrene PS,polyvinylidene fluoride PVDF, and other, mostly synthetic polymers[1-4]. As an alternative to electrospinning, SBS processing parameters make it a versatile method to be used for the production of polymeric nanofibers, havingan advantage in a higher production rate of materials, while all types of solvents can be used [1]. A syringe pump delivers a polymer solution to a system of concentric nozzles passing through the inner nozzle whileahigh-velocity gas flow is sustained through the outer nozzle having a complex ejecting action on the solution which, depending on the process conditions, may generate fibers when the solvent rapidly evaporates. At a certain distance from the nozzle, the fibers are collected on a substrate, usually a rotating drum,forming a nonwoven mesh [1].

In this work, the preparation of materials using SBS from cellulose acetate is presented. Cellulose is the most abundant natural polymer in the world and important in terms of its use as a biodegradable polymer[5]. However, it has very low solubility, while its ester, cellulose acetate, has excellent solubility in common organic solvents. Therefore, acetate is a preferred derivative to be used for processing and has been used for the production of conventional fibers and films, with good transparency and mechanical properties[5].The preparation of cellulose acetate materialswas performed using a homemade SBS device developed at the Department of Materials Science and Engineering at UC3M, Madrid, Spain[3]. A polymer solution of 12% (w/v) was prepared by dissolving commercial cellulose acetate powder in a mixture of solvents (v/v) containing acetone and N,N-Dimethylformamide (DMF). The transition of the produced material from film to a nonwoven fibrous membrane is achieved by increasing the acetone share in acetone/DMFmixture, while other processing parameters of SBS (distance of the nozzle from the collector, air pressure, and injection rate of polymer solution) were kept constant.Changes in morphologywereinvestigated with an optical profilometer. Wettability was evaluated through contact angle measurementsupon contact of the material's surface with deionized water, resulting inhighercontact angle of 105 ± 5.5 ofa nanofibrous membrane, in comparison with a contact angle of 73.5 ± 4 of the produced film.

These results present the possibility to produce cellulose-based films and fibrous membranes using SBS technique. The production ofmaterials with increased hydrophobicity has potential applicability in food packaging, especially having in mind the advantageous use of cellulose.In this way, with a simple, high production rate technique, there is a possibility to produce biodegradable material from a natural and renewable resource.

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The effect of filler content on the structure and properties of PVC/Hap and PVC/wood/HAp composites

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The dynamic development of many areas of life has set new requirements for the polymer industry. The properties of the unmodified polymers became insufficient for specific applications, therefore a need arose to develop new materials with unique properties, such aspolymer composites[1].

Poly(vinyl chloride) (PVC) belongs to the commonly used polymers due to favorable properties. PVC dry blends containing many different additives (thermal stabilizers, plasticizers etc.) are used in processing technology [2].PVC is often used for production of composites with natural fillers, including wood-based filler; wood polymer composites with PVC matrix are characterized by favorable functional properties [3].

Hydroxyapatite(HAp) is a phosphate mineral which occurs naturally or may be synthesized. Its structure resembles the building blocks of bones, therefore it is widely used for preparation of biocomposites for medicine application [4].It can also be used to modify the mechanical properties of polymers[5]

The main purpose of our research was to determine the influence of the addition of the ceramic filler (HAp) on the processing and physicochemical properties of composites based on PVC matrix [6].

We examined two types of composites, both based on PVC unplasticized dry blend with different content of ceramic filler.The first onewas PVC/HAp composites obtained using extrusion method. The second type was hybrid PVC composites with 30 wt% of wood flour (PVC/wood/HAp), which have been processed by kneading method in theplastographchamber. The measurements of density,mechanical properties in static tension, Charpy impact strength and Vicat softening temperature were performed. In the case of PVC/HAp composites, we also tested thermal stability and Shore D hardness. The processing properties during kneadig and flammability were determined for PVC/wood/HAp composites.We expected HApto increase the thermal stability, hardness and softening temperature, while reducing the fracture toughness of the PVC composites.

The results showed that the density of PVC/HAp composites increased with increasing concentration of ceramic filler in polymer matrix. It has also been shown that the addition of hydroxyapatite to PVC causes an increase in the Young's modulus while reducing the values of tensile strength and elongation to break as well as impact strength. It was found beneficial effect of HAp on the thermal properties i.e. significant improvement of thermal stability and increase of the Vicat softening temperature. Similarly as in the case of PVC/HApcomposites, the density of PVC/wood/HAp composites increased with an increase in ceramic filler content. The favorable increase of Vicat softening temperature was also noted. The addition of HAp at a concentration of up to 5% slightly caused deterioration of the tensile properties and impact strength of the hybrid composites compared to the HAp-free composite. The increase of HAp content to 10%, lead to enhancement of Young's modulus and tensile strength values.All composites were non-flammable.

We confirmed the possibility of producing composites based on unplasticized PVC by these methods.The obtained results do not allow for unequivocal determination of the influence of the addition of HAp on the mechanical properties in static tensile and impact toughness of the composites.The discrepancies may indicate a heterogeneous structure of the composites due toinhomogeneous dispersion of HAp in PVC matrix or agglomeration of filler particles.The studies on the evaluation of the structure of the composites and further on the determination of the optimal composition of PVC-HAp blends and the conditions of their processing are required.

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Montmorillonite-*graft*-polyacrylamide hybrid particles for control of the intermolecular interactions within EPDM/MVQ blends

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In this work, interactions between montmorillonite-*graft*-polyacrylamide (Mt-*g*-PAm) hybrid particles and the individual components of immiscible ethylene-propylene-diene modified with sorbic acid (EPDM) and methyl vinyl silicone (MVQ) blends were investigated. Polyacrylamide (PAm) chains were grafted from montmorillonite (Mt)surface via surface-initiated atom transfer radical polymerization (SI-ATRP) to provide polymer brusheswith varied PAm length and grafting density. The effect of various lengths and grafting densities of PAm chains was correlated to particle location in blends and to mechanical and viscoelastic properties of blends.

Number average molecular weight (M_n) and molecular weight distribution ($Đ$) of PAm were determined by gel permeation chromatography (GPC). Molecular weight of PAm was used together with the results of thermogravimetric analysis (TGA) to calculate grafting densities of hybrids.Morphology of the blends was analyzed using optical and scanning electron microscopy (SEM). Crystallinity of MVQ blend component was studied by X-ray diffraction (XRD). Blends were characterized by melt rheology in shear mode, dynamic mechanical analysis (DMA) in tensile mode and broadband dielectric spectroscopy (BDS).

The results showed the chemical nature of polymer brushes controls the particles location in blend, while architecture affects the dynamics of the polymer matrix. Grafting of polyacrylamide chains from montmorillonite resulted in better dispersion of Mt-*g*-PAm in EPDM/MVQ blends in comparison to neat montmorillonite. Due to dipole-dipole interactions and hydrogen bonding generated between carboxyl groups of modified EPDM and amide groups of PAm grafted from montmorillonite surface, Mt-*g*-PAm particles were selectively located at the EPDM/MVQ interphase and in the EPDM phase. Addition of longer Mt-*g*-PAm hybrid particles caused an increase of the glass transition of EPDMand reduction of crystallinity of MVQ phase.The long brushes suppressed the movement of the compatible blend component thank to entanglements, while on the other hand the short dense brushes facilitated the movement of the polymer matrix chains.

In conclusion, precisely designed polymer brushes could be considered as novel functional compatibilizers that control blends' properties, whereas identification and justification of the interactions generated within the blends' component open new perspectives for future material designing.

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Enhancing Tensile Properties of Nanofibrous Membranes by Inter-Fusing Techniques

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The electrospinning process product is typically a nanofibrous layer characterized by high flexibility and large surface-to-volume ratios with specific strength properties depending on the type of material, morphology, and structure. The nanofibrous layer can be used in a wide variety of fields, and the mechanical properties of nanofibers, including the tensile strength, are critical concerning the final application. In this study, to increase the nanofibrous membrane's tensile properties, after the production of nanofibers from polyacrylonitrile (PAN) polymer, immersion methods in dimethylformamide (DMF) solvent system, spin coating, and polyvinyl acetate (PVAc) electrospraying were performed on the membrane to create inter-nanofiber fusing. The samples that have been electrosprayed with PVAc were dried in two ways in the oven, and fusing was performed between nanofibers. The immersion time in DMF was 5, 60, and 120 seconds in which in all the tensile strength improved compared to the as-spun membrane. In the sample immersed 5 seconds in the DMF, the oven-dried spin-coating, and the fused electrospray sample, the tensile strength at break was increased to 176%, 86%, and 88%, respectively. The lowest strain reduction was observed for electrospray samples (1%), and the highest modulus enhancement was for the 5-second sample immersion in DMF solvent system (161%). This simple technique can open the way for adjusting the tensile properties of the membranes according to the application needs.

Graphene Impact in Tensile Properties of Carbon Nanofibrous Yarns

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Carbon yarns, due to their unique mechanical and physical properties such as remarkable strength and high modulus, high fatigue strength, low weight, very low thermal expansion coefficient, high thermal stability, good electrical and thermal conductivity, have been used in the major industries of the world[1]. Increasing its surface area could enhance its properties. In this research, polyacrylonitrile has been used as a precursor of carbon nanofiber yarn, and graphene wasused to improve its mechanical properties. We produced nanofibrous yarns with different percentages of graphene continuously using the electrospinning technique with two opposite nozzles.The nanocomposite polymeric yarns were converted into carbon nanofibrous yarns after controlled stabilization and carbonization processes.The carbon structure and the retention of covalent bonds in the nanofiber yarn during heat treatment improved its mechanical properties.The effect of two factors of heat treatment processes and graphene on the tensile strength were investigated.The amount of applied tension in the stabilization stage caused the nanofibers to be parallel to the axis of the nanofiber yarn and improved its mechanical properties.In carbon yarns with different percentages of graphene,the strength increased by 357% and the modulus by 54 times compared to the polymeric yarn before the heat treatment procedures. The optimal dispersion of graphene in the structure of nanofibers is one of the factors affecting the mechanical properties of composite yarns [2]. In this study,the sample with 0.5 wt.% of graphene with a strength of 28.42 cN / tex and the 1970 cN / tex modulus showed the best tensile propertiescompared to other samples.In this sample, the addition of graphene increased its tensile strength83.43% compared to the carbonized sample without graphene.These nanofiber carbon yarns have potential applications in the manufacture of high-strength composites in a variety of industries, including aerospace, shipbuilding, medical devices, as well as flexible supercapacitors.

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Influence of the injection moulding processing parameters on properties of gear grade PA66 reinforced with glass, carbon or grind carbon fibre and lubricated with PTFE

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The main factors in improving the performance of materials and correspondingly broadening the range of their applications, for example, replace metal with polymeric gears, are optimization of processing and material composition, for which detailed knowledge about material behaviour is fundamental. With this purpose, three ternary composites each containing 30 wt.% of either glass fibre, carbon fibre or milled carbon fibre and lubricated with 15 wt.% polytetrafluoroethylene (PTFE) were injection moulded using the recommended parameters. Additionally, ternary composites were processed under 8 different combinations of processing parameters, with five factors at two levels, according to the Taguchi L8 orthogonal array. Studied factors were melt temperature, tool temperature, injection speed, screw rotation speed and backpressure. Mechanical and thermal properties of samples were characterized using a tensile test, flexural test, Charpy impact test, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Hot Disk method. The topological properties of samples were evaluated using surface roughness measurements. The tribological properties of samples were characterized using the Pin-on-Disc method. Additionally, failure analysis of tribologically tested specimens and counterparts was performed using optical microscopy (OM). It has been found that the variation of processing parameters had the highest impact on GF reinforced composites. In most cases, the melt temperature had the highest impact on the modulus and strength of the composite, where higher temperatures resulted in increased values. Surface roughness was most affected by the injection speed and tool temperature, where higher values of both factors resulted in smoother surfaces. Moreover, the influence of processing parameters on surface roughness was at least as significant as the material composition.

PVA/rGO aerogels preparedby modified room temperature freeze gelation method

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Aerogels are a large class of materials with a porous structure, which consistof more than 90% of the air and therest is a solid backbone.Due to their unique structure,these materialsshow very low density and large specific surface area. Recently a lot of attention has been paid to aerogels based on carbon nanomaterials like graphene or carbon nanotubes. One of the most promising advantage of the carbon and graphene aerogels is the possibility of tailoring their physicochemical properties. For instance, the pore size can be control by optimization of synthesis parameters or blowing agent.Furthermore, the use of different carbon precursors can promote forming of hybrid aerogels with polymers or inorganic substances.These unique properties of aerogels made them an object of intense research interestin many fields of science and industry like: medicine, electronics, construction applications or environmental protection[1, 2].

With the development of research on carbon aerogels, a number of their preparation methods have been described, i.e.: hydrothermal reduction, chemical reduction, template assisted method. One of them is based on the synthesis route called room temperature freeze gelation (RTFG). This method was first described by Halloran and co-workers and used in the ceramics industry [3]. Lin et al.utilized this process to obtain nanocarbon aerogels. In this work, different carbon starting materials (pristine graphene, graphene oxide, and others), weremixed with an appropriate solvent (phenol and camphene) above theirmelting point, and then samples were solidified by freezing to form a stable shape. Solvents characterized by a high vapor pressure at room temperature are selected, becausethey can evaporate at RT leaving a porous structure in the starting material [4].

In the presented work, the above-described RTFG process after modification was used to obtain polymer-carbon aerogels. The selectedpolymer was polyvinyl alcohol (PVA).The role of PVA was to improve the dimensional stability of the materials. Samples with variouscarbon to polymer ratioas well as different carbon concentrations (C_c) of the starting suspensions were obtained. The effect of these factors on the structures and pore sizes of the obtained materials were observed using scanning electron microscopy (SEM) (Fig.1.). X-ray diffraction and Raman spectroscopy measurements were also performed to study the crystalline lattice parameters and structural order degree of the obtained porous materials.

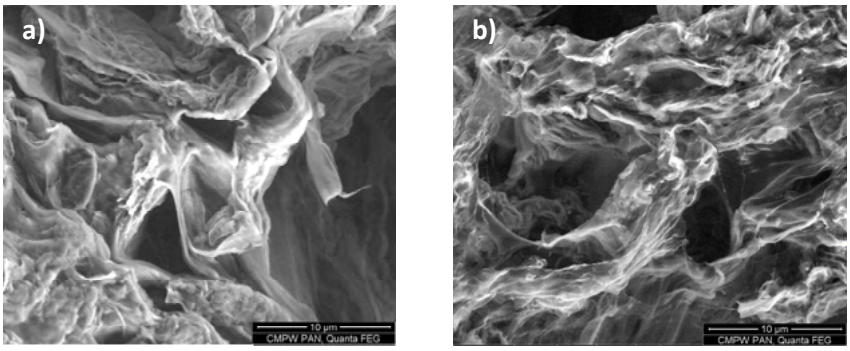

Figure 1: SEM microphotography of a) rGO/PVA 30/70 C_c= 100 mg/ml and b) rGO/PVA 30/70 C_c = 50 mg/ml

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Graphene Oxide as a multifunctional additive to polymer composites

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Graphene is a material that has attracted a lot of interest in the 21st century due to excellent mechanical, thermal and electrical properties. Very recently a lot of attention has been focused on graphene derivative; graphene oxide [1].

Graphene oxide has a monolayer structure in which carbon atoms forma hexagonal network with sp^2 hybridization. Modification of graphene with oxidizing agents such as sulfuric acid (VI), potassium manganate (VII) enables the introduction of hydroxyl, carboxyl, or epoxy groups into the graphene structure. The advantage of having the above-mentioned functional groups is the possibility to modify the graphene oxide, that provides new properties of that material. Both, covalent or non-covalent methods are used for graphene oxide modification. A relatively new approachrelies on the grafting polymers from the graphene oxide surface.That can be done via atom transfer radical polymerization (SI-ATRP) technique [2]. As a result organic inorganic particles are obtained.

The addition of particles containing graphene oxide with a grafted polymer to the polymer matrix generates interesting properties of obtained composite. First of all, it is possible to achieve satisfactory mechanical and/or electrical properties that would be impossible for a homopolymer alone [3].

In this presentation, strategies used for graphene oxide modificationas well as the properties of generated polymer composites will be presented.

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Alginate gels with modulated hydrophobia properties

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Over the last years, new approaches for the synthesis of hydrogels have been employed, in particular supramolecular interactions have recently been introduced to build different high-strenght hydrogels that present better mechanical properties and to closely match the mechanical properties of natural tissues [1].Self-assembly of copolymers with hydrophilic and hydrophobic domains for the formation of hydrogels constitute one of the most common approaches to yield hydrogels with improved mechanical properties. When the hydrophobic domains present a semicristalline nature, they can act as junction points in the gel giving rise to semi-crystalline gels.The main characteristic of physical and semi-crystalline hydrogels is that, at the melting temperature, the mechanical properties change reversibly from a solid state to a liquid state. This feature allows the use of these materials for 3D/4D printing[2]. Semicrystalline physical hydrogels have good mechanical properties and at a high degree of crystallinity, they exhibit a high Young's modulus and sustain tensile stresses up to 7 MPa. However, they are brittle under tension and rupture at a few percent of elongation. To improve their tensile mechanical properties, the mixed-hydrophobe technique was recently developed which is based on the use of strong and weak hydrophobic monomers and polymers together in the gel preparation [2]. Hydrophobic domains increase tear, shear and creep strenghts compared to traditional hydrogel due to their characteristics they are used, for example, as a substitute for cartilage [3].

The aim of the work is to develop novel hydrogels with modulated hydrophobia properties based on sodium alginate, an hydrophilic polysaccharide widely employed in biomedical applications. To that aim, alginate was first grafted with octylamine and the chemical structure was fully elucidated through spectroscopic techniques. Then, the modified alginate was combined in solution with polybutylensuccinate, a semicristalline biobased polyester and the formation of alginate/PBS gels was explored as a function of PBS and alginate concentration. Finally,the obtained gels were fully characterized through oscillatory rheology[4] in order to evaluate their potential application as biomaterial inks for 3D printing.

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Smart Nanoparticles: Responsivity Analysis using Field Flow Fractionation

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Smart and biodegradable polymers form the foundation of future research on advance nanoparticles (NPs) for drug delivery systems. Amphiphilic block copolymers that self-assemble into nanoparticles, particularly polymersomes, are versatile carriers due to their colloidal stability, mechanical properties, controllable membrane properties and ability to enclose a broad range of drugs, enzymes, and other functional molecules [1]. Smart polymers in amphiphilic block-copolymer forming nanoparticles are stimuli-responsive that can impart a change in structure or morphology upon application of a specific stimulus. More complex structures have been developed to respond to the presence of multiple stimuli such as dual-responsive polymersomes (temperature and pH responsive) that assemble and disassemble depending on the lower critical solution temperature (LCST) and characteristic pH-switch value of the respective polymers [2]. The separation and characterization of such complex self-assemblies proves to be a challenge due to their polydisperse nature with a broad range of expected sizes and shapes and the possible decomposition under strong shear forces. These limitations exclude the application of size exclusion chromatography (SEC). Asymmetric field flow fractionation (AF4) is an emerging technology for detailed separation and characterization of complex self-assemblies. This technique allows for gentle separation of several analytes in a thin channel without packing material which provides low shear and low-pressure conditions that are key to preserving the structure and aggregation of delicate self-assemblies [3]. AF4 allows for a fast change of eluent without long equilibration times as is the case in SEC packed columns. The channel is situated in a temperature-controlled oven which creates the possibility of temperature analysis. Consequently, the pH and temperature dependence of dual-responsive polymersomes can be investigated using AF4. Hence, polymer separation using field flow fractionation can be applied to estimate the dispersity and effectiveness of both – the pH switch point and the LCST behaviour of polymers and their self-assemblies.

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Thermal aggregation of HEMA-OEGMA copolymer in the DMEM medium and its salt solutions

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The formation of nanostructures called mesoglobulesin dilute aqueous solutions has been studied for many temperature responsive polymers [1]. Process of polymer chains aggregation to nanoparticles above critical temperature depends on number of factors: the concentration of the solution, its heating rate, molar mass of polymer and the presence of substances added to the solution, like surfactants or salts [2].

In human body fluids there is quite stable concentration of various components like salts, amino acids and others[3]. The study of thermoresponsive polymer behavior in solutions of body fluids componentsis crucial for the use of these polymers in medical applications. The determination of size of the thermaly induced aggregatesand their stability over time is vital under physiological conditions.

In case ofthermoresponsive polymer solutions with salts, the literature focuses on determining the effect of salt presence and its concentration on the transition temperatures [4]. There are practically no studies describing the formation of particles in such solutionsand containing information about particles` sizesand stability over time.

The presented work encompassesinvestigation of the thermal aggregation of thecopolymer belonging topoly[(2-hydroxyethyl methacrylate)-co-oligo(ethylene glycol) methyl ether methacrylate][P(HEMA-co-OEGMA)] family.The response of P(HEMA-co-OEGMA) to temperature could be adjusted in the range from 66.5 °C to 21.5 °C by changing the HEMA content [5].For the purpose of our studies copolymer with 90% HEMA and T_{CP} of 25,5 °C was used. The temperature behavior of the copolymer were performedin cell culture medium DMEM as well as in solutions containing single salts and aminoacids from DMEM whose concentration is the highest.

The light scattering method and UV-Vis spectroscopy were used to followthe process of mesoglobules formation and their behavior in solution.Low molar mass substances have been shown to affect not only transition temperatures but also particle size and their stability over time. Studies confirmed that inorganic ingrediencies influenced the particles formation more significantly that organic substances (Fig. 1). Size of mesoglobules in most of this solutions were not stable and additional aggregation occurs.

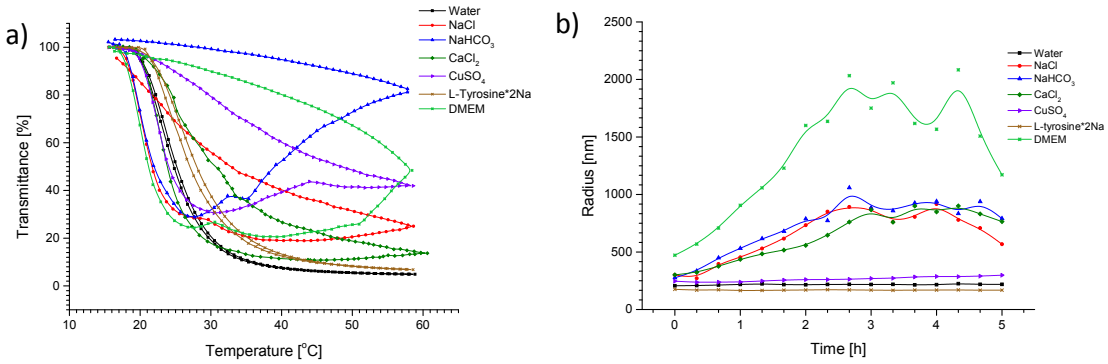

Figure 1: a) Transmittance of HEMA-OEGMA copolymer solution (C=0.5 g/L) vs. temperature, b) Particle size changes during incubation of dispersion at 55 ° C.

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Why the reported lower critical solution temperature (LCST) values of thermoresponsive polymers are not the LCSTs but only the critical solution temperatures (CSTs) for a given condition

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Responsive (intelligent, smart, adaptive) polymers, their gels and nanostructures are intensively investigated worldwide nowadays. Among these macromolecular materials, thermoresponsive polymers, possessing a critical temperature in term of their solubility, have gained outstanding interest. However, when reliable comparison of the reported data on the critical solubility temperature is attempted, it has turned out that this seems to be an impossible task [1], on the one hand. On the other hand, it was found by us that surprisingly a vast number of authors report the result of one single experiment with a selected single condition as the lower critical solution temperature (LCST) for the investigated polymers in spite of the fact that the LCSTis defined as the minimum of the critical solution temperature (CST) versus volume (mass) fraction of polymer solutions.The same holds for USCT-type (upper critical solution temperature) polymers as well.

Therefore, it can be concluded that independent of the applied method, such as cloud point and clearing point determination by turbidimetry with UV-vis spectroscopy, IR or NMR spectroscopies, DSC and DLS, the results with one single polymer concentration under a selected condition have been erroneously reported as LCSTs, that is, these are not the LCST values. Instead, these are the critical solution temperatures (CSTs) of the examined polymers for only the investigated conditions [1,2]. As our systematic experimental investigations with poly(N-isopropylacrylamide) (PNIPAAm), the most widely studied thermoresponsive polymer, show, even the CSTs depend on the experimental conditions, such as the polymer concentration, heating/cooling rate, equilibration time between temperature change, the wavelength of the light when turbidimetry(transmittance by UV-visible spectroscopy) is used for CST determination, and the way of data evaluation as well. In relation to this later problem, the unreliable onset, 5%, 10% or 50% change in the data have been reported as CSTs (cloud points or clearing points by turbidimetry), worst as LCSTs or UCSTs, in the vast majority of the cases. In order to obtain comparative, standardizable critical solution temperature data all over the world, a simple set of experimental condition for CST determination of thermally responsive LCST-type and UCST-type polymers is proposed by us:

(1) measure the critical solution temperature (CST) of a 0.1 wt% polymer solution;
(2) use 0.2 °C/minheating/cooling steps with 5 min equilibration between the gradualchange of temperature;
(3) forturbidimetry measurements, apply 488 nm wavelength to obtain datacomparable to light scattering at this wavelength;
(4) determine the critical solution temperature (CST) asthe***inflection point*** of the transmittance (absorbance)-temperature curves obtained by turbidimetry (cloud point or clearing point), or by any measured thermoresponsivedata by other techniques, such as IR and NMR spectroscopies, DLS etc.), and ***not*** the unreliable onset, 5%, 10% or 50% change in the data;
(5) measure the hysteresis with all thermoresponsive, and responsive (intelligent, smart, adaptive) polymersin general, in all cases, due to the importance of the reversibility of the response behavior from both scientific and application point of views.

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Advanced characterization of rubber compounds based on a novel unified physical framework for different experimental approaches

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Elasticity in rubber materials depends on different molecular parameters that define the network structure. Crosslinks and entanglements have an effect that is already considered in different ways in the diverse rubber elasticity theories. Different experimental approaches to characterize those parameters are mechanical tests, swelling experiments and more recently double quantum nuclear magnetic resonance (^{1}H DQ-NMR, see **Figure 1**) [1]. The analysis of those experiments is based on different assumptions and theoretical approaches, reducing the consistence of the so-obtained results.

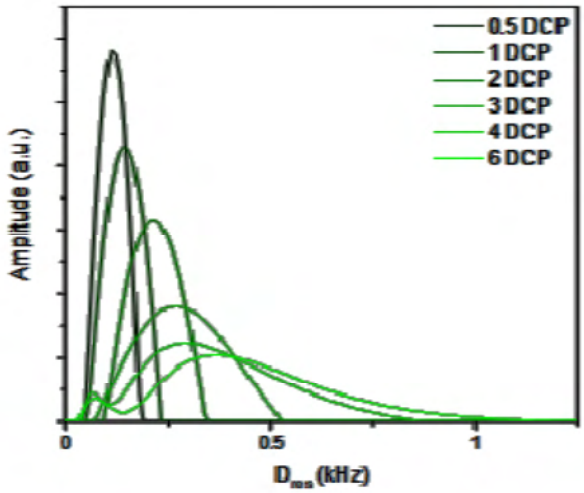

Figure 2: Distribution of residual dipolar coupling frequency as a function of DCP fraction.

The main purpose of this work is to unify for the first time those approaches in order to work under just one physical framework as independent as possible from the experiments. This will lead us to a new methodology for the analysis that allows to combine those experimental techniques for a better quantification of structural parameters as crosslink and entanglement density. Moreover, it could set the effect of other important parameters as network defects (dangling chain ends and loops) and spatial distribution of crosslinks (not considered in the rubber elasticity theories) in the physical properties of rubber materials [2].

Finally, the new methodology could be used to characterize filled compounds. These technological relevant products are a complex challenge for quantifying the key-parameters that define their structure. In this sense, there are some effects that are not able to be independently quantified by using a unique experimental approach, such as the matrix overstrain or filler-rubber interactions. The knowledge of those effects and the quantification of them attending to a physical model based on statistical mechanics will provide more accurate molecular parameters that define the network rubber structure in technological relevant rubber compounds.

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Characterization of glycopolymers by asymmetric flow field-flow fractionation

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Asymmetric flow field-flow fractionation (AF4) is an advanced analytical tool applied to study the interactions between human serum albumin (HSA) and dendronized glycopolymers. Dendronized polymers (DenPols), surrounded by a maltose shell provides an abundance of hydrogen bonding sites that are favourable for interactions with HSA. The challenge with the characterization of DenPols is the ultrahigh molar masses and the molecular heterogeneity. For this study two different DenPols were evaluated, lysine maleimide DenPols (MI-G0-MAL – MI-G3-MAL) and poly (ethylene glycol), (PEG) maleimide DenPols (MI-G1-PEG-MAL). AF4 allows for gentle separation and therefore ideal for the characterization of DenPols, HSA and the complexes formed by the interactions between DenPols and HSA. Dynamic light scattering (DLS), size exclusion chromatography (SEC) and AF4 were applied to investigate the molar mass distribution, radius of gyration (R_g), dispersity, hydrodynamic radius (R_H) and molecular architectures of these ultrahigh molar mass DenPols. The study showed the pronounced aggregation of the DenPols in the phosphate buffer. AF4 revealed the aggregates present as elongated (rod-like) or spherical and the individual macromolecules as a random coil conformation. After the complex formation between DenPols and HSA, a deviation in the aggregation mechanism of the DenPols observed. The conformation of the aggregated structures of the complex having hard dense spherical and swollen macromolecular architectures. The increased availability of hydrogen bonding sites surrounding MI-G3-MAL had a large impact on the conformational changes with the introduction of HSA. The multivalent interactions between DenPols and HSA were obvious in this study indicating tunable aggregation and conformation of the DenPols.

Polydimethylsiloxane Based Sorbents for Oil Spill Cleanup

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Since the development of oil and chemical companies, industrial waste materials have been causing pollution in the oceans and seawater as a result of both transportation and accidents, even today [1, 2]. In terms of water pollution elimination, physical (booms, skimmers, absorbents), chemical (dispersants, solidifiers), and biological (bioremediation) methods are currently being developed by scientific researchers and applied in the industry [3]. Among these methods, the use of absorbent organogels stands out, with regards to their high absorption capacity, durability and reusability [4].

Organogels are three-dimensional cross-linked structures that interact with organic solvents and absorb these solvents at a high rate, relative to their volume. Polydimethylsiloxane (PDMS)has been utilized as a sorbent material because of its hydrophobicity, buoyancy, chemical stability, and flexibility [4].

With this developed strategy, an organogel with high selectivity forcrude oil and gasoline, as well as petrochemical materials such as BTEX solvents was produced with PDMS macromonomer and appropriate cross-linker. Fabrication of the sorbentwas carried out via bulk polymerization in the absence of solvents, initiators,andcatalysts. Within the scope of the study, the absorption capacity was examinedby changing the molecular mass and the cross-linking ratio of the macromonomer in the presence of various solvents. Absorption/desorption kinetics was analyzedand swelling tests have been implemented with the consideration of shaking rate, various water mediums, and reusability.

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Isolation and characterization of important bimodal HDPE components: A comprehensive study using advanced analytical techniques

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To enhance performance, polymers are often made as blends/alloys of different components serving different purposese.g., ease of processing or robust mechanical strength. To achieve this, a multi component reactor/catalyst system is often used. However, this creates unique challenges in the separation and quantification of the inherent components to evaluate both catalyst and synthetic competences. Polyolefins are a unique and increasingly important sub-section of the global thermoplastics market. Ethylene-based polyolefins make large portion of the thermoplastics market and are easily designed for robust purposes such as in the case of bimodal high-density polyethylene (bHDPE) [1-4].The presence of multiple components creates challenges in characterization which requires a multiple fractionation protocol. Firstly, important components are fractionated using preparative temperature rising elution fractionation (p-TREF).

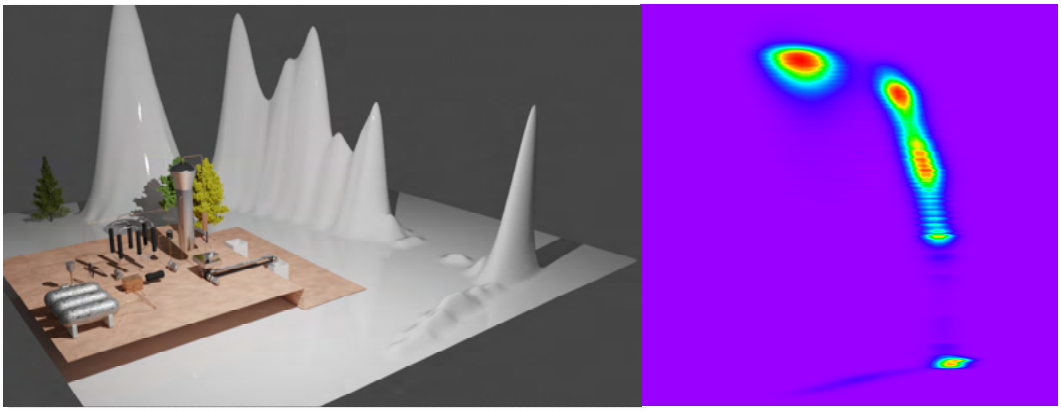

Figure 1. Separation of a bHDPE low temperature p-TREF fraction using high-temperature two-dimensional liquid chromatography (HT-2D-LC).

In the present work, several high temperature interaction chromatography (HT-IC) techniques are used to separate low molar mass components from the copolymer is the lowest temperature fraction (70 °C). HT-IC is compared to high temperature size exclusion chromatography (HT-SEC) and successive self-annealing fractionation (SSA). This approach eliminates the need to analyse all the fractions in great detail since major differences regarding the synthetic process e.g., efficient comonomer addition or molar mass control can be revealed in a multicomponent fraction.

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Recent progress in interaction chromatography of ethylene-based polyolefins

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Polymers are complex materials which require characterization after synthesis or post-synthesis modification process. Polyolefins (POs) today constitute a large percentage of the plastics market and can be easily modified into niche products for tailored use. Interaction chromatography of POs at high temperature (HT-IC) is an exciting technique for the characterization of polyolefins. In comparison to other techniques used for describing the chemical composition (CC), HT-IC accommodates functionalised and non-functionalised polyolefins as well as a broad range of crystallinities [1, 2]. This means non-crystallinePOs exhibiting high levels of branching can be analysed simultaneously with highly crystalline materials of the same family/catalyst origin. For complex polyolefins, complex solvent systems and/or complex stationary phases must be developed to exploit the inherent attributes of the semicrystalline materials such as ability to crystallise from solution and to adsorb onto porous graphitic carbon (PGC).

Linear low density polyethylene (LLDPE)and low molar mass polyethylene (PE) serve as excellent starting points for establishing and improving analytical protocols for the separation of copolymers, branched and hyperbranched polyolefins. In the present poster, we present our recent work which illustrates ways in which existing HT-IC protocols in solvent and temperature gradient modes (HT-SGIC and HT-TGIC respectively) can be improved. The first part introduces the use of a two-column set-up in series in a single oven for the separation of oligomers while the second part explores a multi oven set-up for the separation of high molar mass PEs with low levels of branching [3, 4].

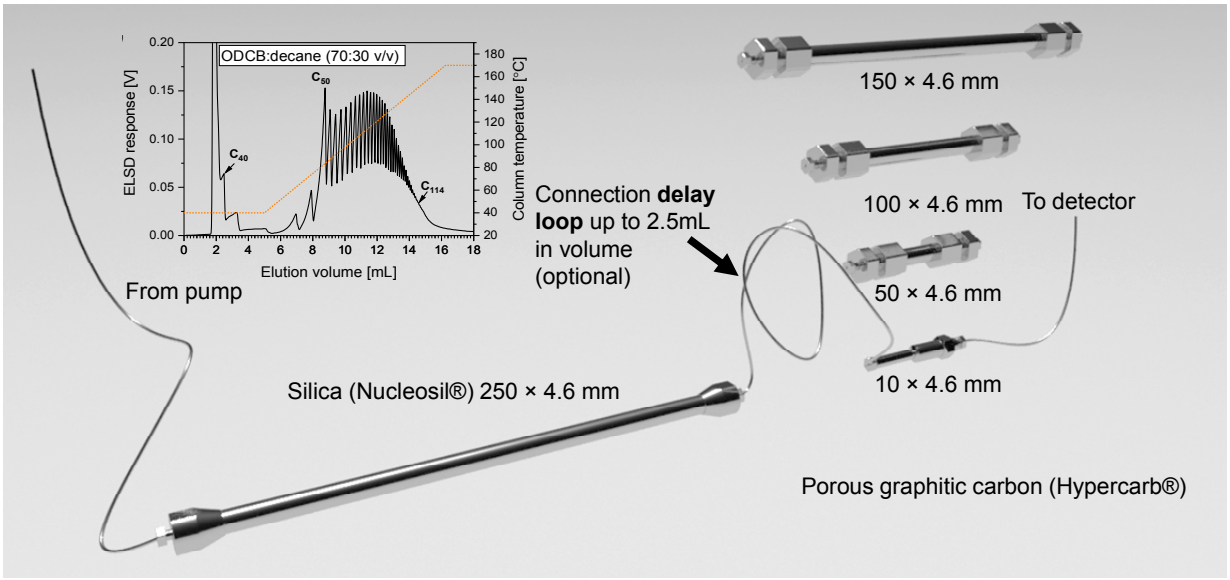

Figure 1. Utilising an adsorptive and a non-adsorptive column for the separation of polyethylene oligomers under temperature gradient interaction chromatography conditions.

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Synthesis of polyurethanes based on diol - 2,6-di (1-phenyl-5-hydroxy-1H-pyrazol-3-yl) pyridine with spin-crossover effect

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The past decade many scientific papers of researches SCO-compounds have been published. They are demonstrating the great potential of using these smart and multifunctional materials, which are able to effectively change their magnetic, optical, electrical, thermal and mechanical properties. Because of external disturbances (temperature, pressure or radiation) SCO complexes are capable of undergoing a spin transition, i.e. reversibly switch between low-spin (LS) and high-spin (HS) states [1]. The transition between these two states is accompanied by significant changes in magnetic and optical properties, some of which (color change) can be observed with the eye. The combination of SCO-compounds and polymers makes it possible to achieve a variety of shapes and sizes (from nano to macro level), which is also promising in various fields of application: sensors, actuators and energy conversion and storage devices.

Most of the scientific works are devoted to polymer composite materials, in which the polymer acts as a matrix, the spin-transition complex - separate phases [1]. However, no information has yet been provided on the polymer, in the structure of which the SCO-complex is already included.

The work presents the synthesis of three new polyurethanes (Fig. 1) based on diol - 2,6-di (1-phenyl-5-hydroxy-1H-pyrazol-3-yl) pyridine (L1) and various diisocyanates: hexamethylene diisocyanate (HDI), diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI).

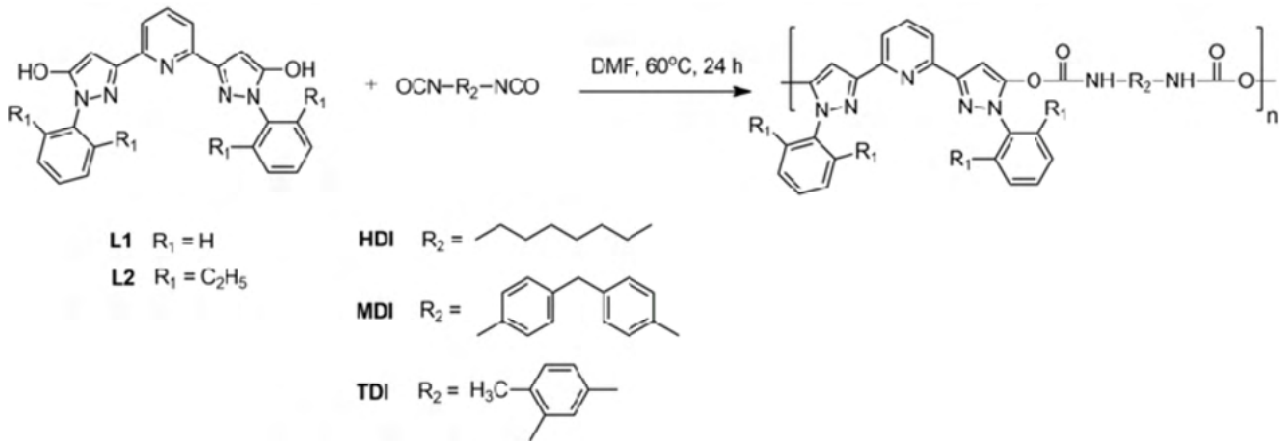

Fig. 1 Molecular structures of synthesized polyurethanes

L2 is capable of forming spin-crossover complexes with the iron ion Fe^{2+}, so obtained polymers are promising for the creation of temperature sensors and pressure sensors [2]. The number average molecular weight of the obtained PUs varies from 42000 to 57000 Da. The thermal properties of polymers were studied by thermogravimetric analysis and differential scanning calorimetry. The possibility of the formation of complexes of polyurethane with the ferrous ion in DMF at room temperature was also shown.

Acknowledgement: The study was supported by a grant from the Russian Science Foundation (project No. 21-73-20117) andthe Competence Center of the National Technological Initiative (NTI) "Digital Materials Science: New Materials and Substances" of the Bauman Moscow State Technical University.

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Synthesis of Polymer Nanocomposites and Their Use as Organic Solvent/Oil Absorbents

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Oil spills and the leakage of organic liquids have caused many vital problems, with almost irreversible consequences.Therefore, these contaminants must be effectively removed from the water surface. Various methods are used to remove dispersed oil and organic liquids from the water surface, such as physical absorption by sorbent materials, mechanical recovery with oil skimmers, in situ burning, physical diffusion, membrane filtration and biodegradation [1].Among these methods, the use of absorbent materials is an attractive approach for the removal of organic liquids from the water surface,due to the high and fast absorption ability and also the reusability of the absorbents [2].

Polymer nanocomposites are an attractive class of materials that improve the performance of materials. Nanometer-sized particles have been prepared from various organic and inorganic particles, and their incorporation into composite materials has shown significant improvement in the mechanical, thermal and electrical properties of polymer nanocomposites [3].Polymer nanocompositesoffer the possibility of developing advanced materials that are effective in many fields by optimizing their properties such as hydrophilicity, hydrophobicity, porosity, and dispersibility [4].Moreover, it is possible to prepare polymernanocomposite sorbents with different functionalities by using different types of polymers and nanoparticles [5].

In this study, polymer nanocomposites were prepared by the condensation of hydroxyl functionaland alkoxysilane monomers at moderately high temperatures in the presence of inorganic nanoparticles.The effects of changingthe nanoparticle ratio oncomposite properties, porosity and solvent absorption were investigated.The characterization of polymer nanocomposites was determined by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA).

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Release kinetics of purpurin from three purpurin-based hybrid pigments

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Polymer materials are currently used in many areas of everyday life. Many applications require the polymer to be colored (toys, jackets of electric cables and optical fibers, office supplies and much more). Color can be given to polymeric materials by adding pigments or dyes. Natural colorants such as purpurin are of particular interest due to its "green" character. Enclosing such dyes on a carrier allows to obtain durable additives for polymer materials.

The photochemistry of fading, bleaching, and acidichromic effect of the purpurin, a derivative of the anthraquinone dyes, have been broadly described in the literature. The photobleaching of purpurin is solely dependent on the ET dynamics of the system [1]. Besides that, another research [2] did handle the measurements of absorption and emission spectra of purpurin in water solutions at different pH conditions, in the presence and absence of light. However, the systematic studiesconsidering the solvatochromic effect observable in absorption and emission spectra of purpurin, as well as, processes of release of purpurin from purpurin-based hybrid pigments have not yet been conducted.The research that is to be presented, does indeed deal with the explanation of solvatochromic effect occurring in the solutions of purpurin dissolved in various organic solvents. Furthermore, the release of purpurin from three hybrid pigments – siral/purpurin, hydrotalcite/purpurin, and sepiolite/purpurin – was examined in organic solvents using UV-vis spectrophotometry. The results of the experiments may shed light on the stability of purpurin under different conditions. What is more, conclusions about various electron transfer mechanisms occurring while those release processes can be made. These can be important in improving and even establishing new applications of purpurin.

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Correlation between H-bonding formation and value of an open circuit potential of symmetrical supercapacitor based on Poly-(3,4-ethylenedioxythiophene)

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The electronic industry and basic research institutions have made enormous effort for the development of easy-fabricated solid-state energy storage devices based on conducting polymersdeposited on flexible platforms such as plastic or C-based substrates [1].Pseudocapacitors have become promising energy storage units due to their much higher energy density compared to conventional capacitors and more elevated value of power density compared to batteries[2, 3].The conjugated polymers are good candidates for pseudocapacitors due to the fast-redox conversion at the surface of the deposited film [4].The general demands for pseudocapacitors are high working(output) voltage, high capacitance, and low resistance for pulse power supply applications.The output voltage of the pseudocapacitorsis generated by the difference of electrical potential of two electrodes. In order to provide a large value of output voltage, the oxidation level of the two electrodes must differ as much as possible (the potential difference of the neutral (undoped) state and oxidized (doped) state).The tuning of redox state and electrical properties of the conjugated polymer can be achieved, for example, by utilization of protic acids.The interaction of polymer chains with protic acid by H-bonding provides the changing of structure and assembling of polymer chains, as was recently shown by us[5]. The objective of this study was to fabricate a PEDOT-based symmetrical supercapacitor (Fig. 1) withhigh and stable in time value of an open circuit potential (V_{oc}). In addition, it has beendemonstratedthe roleof H-bonding on thevalue of V_{oc} for the symmetrical supercapacitor [6].

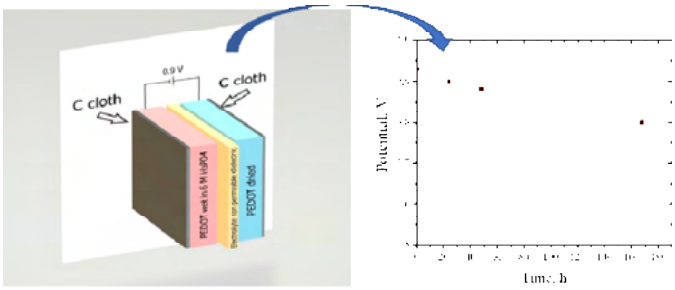

Figure 1. Schematic illustration of the symmetrical supercapacitor device based on PEDOT electrodes (left) and stability of an open circuit potential in time (right)

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Electron Transport in Naphthalene Diimide Derivatives

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In the eighties of the twentieth century, interesting electrical properties of arylene diimide derivatives were noticed. With the development of modern organic electronics, interest in these materials is growing. Currently, there are reports of the use of these materials in n-channel organic field effect transistors or as an acceptor component of bulk heterojunction in organic photovoltaic cells.Also, the various naphthalenediimide derivatives can be used in the organic photovoltaic cells, organic photodiodes, and organic light emitting diodes as an electron transporting interlayer.

In our research, we focused on the study of electron transport in two naphthalene diimide derivatives, namely, N,N'-bis(sec-butyl)-1,4,5,8-naphthalenetetracarboxylic acid diimide (NDI-s-Bu)[1] and N,N'-bis(4-n-hexyloxyphenyl)-1,4,5,8-naphthalenetetracarboxylic acid diimide (NDI-4-n-OHePh)[2].

DC tests for electron-only devices with diimide layer sandwiched between the ITO and Al electrodes were carried out in an inert atmosphere of a glove box. The research has shown that NDI-s-Bu and NDI-4-n-OHePh are strongly unipolar, being characterized by good electron transport properties and essentially negligible hole transport. The obtained current–voltage characteristics were analyzed by applying the drift–diffusion current modelfor low voltagesandfor higher voltage the Mott-Gurney model of space charge limited current were used.Fitting the experimental data to these models yielded the electron mobility of 4.3×10^{-4} $cm^2V^{-1}s^{-1}$ and 4.6×10^{-6} $cm^2V^{-1}s^{-1}$ for (NDI-s-Bu) and (NDI-4-n-OHePh), respectively [3].It was also shown that the use of two blocking electrodes and the injection of charge carriers (instead of one ohmic and the other blocking) allowed for a reliable analysis of the experimental current-voltage characteristics in electron-only devices using the original version of the drift–diffusion–current model.

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Optically-triggered junctions for polymer-based organic electronics: A computational study

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Molecular switches based on azobenzene (azo) are defined as light-responsive molecules which can change between two configurational states under light stimuli. Responsive azo monolayers can be used to modulate the work function, i.e. they tune the properties of the interfaces – at the electrodes or nanoparticles. In this work, we investigate what happens to the structures, optical properties, and the charge hopping within azo-bithiophene (azo-BT) hybrid monolayers depending on the light stimulus using various computational approaches.

Two types of hybrids that differ in the order of azo and BT counting from the anchor group are modelled: azo-BT and BT-azo. One of them (BT-azo) has been studied experimentally by Karpe et al. [1], whose data are used for the model validation. We describe trans- and cis-isomers for each hybrid and conclude that the isomers of BT-azo are more stable. The optical spectra for trans-isomers are similar, whereas the cis-states are characterized by different positions and intensities of the absorption bands. The charge hopping is evaluated for the coupled dimers within Markus-Hush theory of electron transfer.

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Synthesis of the dopamine based molecular glue

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With the fast-paced development of new medical procedures for skin treatment, physicians have encountered a problem with the lack of suitable polymeric materials. The investigated biocompatible molecular glue, containing catechol groups to increase the adhesion properties, is based on the structure of the marine mussels' byssus. With the use of the polyphenolic proteins on the byssal plaques, mussels are able to adhere strongly in the humid environment. The possibility of mimicking the behaviour of byssi allowed the creation of the adhesive polymer, with poly(isobutylene-alt-maleic acid) backbone and dopamine side chains, as the catechol group donors. The investigation was held to analyse the controllability of the addition of the amount of dopamine into the polymer chain. The UV-Vis spectroscopy and Dynamic Light Scattering analyses were used to assess the solubility of the material in water and phosphate-buffered saline (PBS). Further investigations of the material will focus on the evaluation of adhesive properties the selected dopamine – to – polymer unit ratios, as well as on the examination of the biocompatibility of the glue.

Rheo-optical studies of the molecules conformation during the injection application of thermosensitive polysaccharide based-hydrogels

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Recently, the biomedical engineering field has seen a growing interest in innovative treatment and regeneration methods. Thermosensitive polymer systems which undergo sol-gel phase transition with an increasing temperature seem to be an interesting solution. This phenomenon is used to design low-invasiveness, injectable scaffolds forming a three-dimensional structure directly inside the body.So far, no studies have been undertaken to determine the effect of shear forces occurring during injection on the spatial conformation of polymer molecules and, consequently, the conditions of matrix formation.

Thermosensitive hydrogels obtained from chitosan and hydroxypropyl cellulose were used as the experimental material.For the latter, powdered HPC was suspended in distilled waterto obtain a 10% (w/w) colloidal polymer suspension.In the case of chitosan systems, the polymer powder was dissolved in 0.1M hydrochloric acid. Next, suspension of disodium β-glycerophosphate (2g of powder distributed in 2ml of distilled water) was added dropwise to the polymer solution.Finally, a 2% (w/w) colloidal suspension of chitosan was obtained, prepared according to the commonly used methodology [1, 2].In order to assess the structural changes of polymer molecules occurring during the injection, three-interval thixotropic tests [2, 3] were carried out with simultaneous small-angle light scattering analysis [4, 5].

It was found that the obtained scattering patterns significantly depend on the intensity of the shear rate in in the second test interval.In the case of chitosan colloids, the increase in shear rate corresponding to the use of smaller needles during injection, a stronger intensity anisotropy along the main and perpendicular directions was observed.This indicates a deformation and orientation of the polymer molecules along the shear field.A further increase in the shear rate additionally resulted in an increase in the area of the recorded scattering signal indicating a reduction in the characteristic dimension of chitosan molecules.A slightly different behavior was observed when HPC was used.Exceeding the shear rate of approx. 3000 1/s resulted in the registration of images comparable to those obtained during multiple light scattering.Moreover, it was found that the chitosan systems return to the initial state after the disappearance of the short-term intense rotational shear interval, while the HPC-based systems undergo irreversible changes.The latter phenomenon may indicate that for some polymers the application of too high a shear field may significantly slow down the phase transition or even prevent the formation of the polymer matrix.

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Synthesis and characterization of acid-cleavable nanogel protein carriers

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Nanogels as three-dimensional nanoscale polymers obtained by physical or chemical cross-linking may be the answer to the issue of selective drug targeting to tumor tissue in effective cancer therapy. They are considered as nanocarriers in drug delivery systems due to unique and beneficial properties such as: high surface area to volume ratio, biocompatibility, large capacity and protective properties for trapped drugs against in vivo degradation. What is more, their design may lead to stimulus responsiveness, and nanogels might react to internal or external stimuli such as pH, temperature, light and redox, thus providing the controlled release of trapped bioactive compounds. This feature may provide the control of the release of biologically active compounds when administering drugs in nanogels as carriers, as they can respond to factors, e.g. when administered parenterally, in blood plasma and in intercellular fluid (pH 7.0 – 7.4) remain in their original form, and after cellular uptakein acidic conditions of lysosome (pH 4.5 – 5.0)undergo degradation.

This work reports synthesis of degradable nanogel carriers with acid-cleavable cross-linker based on benzylidene acetals of trehalose. Nanogels were obtained through inverse miniemulsion polymerization with photoinitiation. The obtained products were characterized using DLS technique and TEM imaging, thereby obtaining information about the hydrodynamic diameter (about 265 nm), the polydispersity index (about 0,2) and spherical shape of nanoparticles. Moreover, we investigated the ability of nanogels to degrade in physiologically relevant acidic conditions imitating their degradation in lysosomes (with pH ranging 4.5 – 5.0). Confirmation of the nanogel's ability to degrade at a pH similar to the pH of lysosomes promptedus to carry out the trapping of model protein - bovine serum albumin (BSA) - during polymerization, and to study the protein release profiles under nanogel degradation conditions. The time of full degradation for the tested pH 4.5 and 5 is 48 and 120 hours, respectively, however studies indicate that complete degradation is not necessary to release 100% of the releasable protein.

The effect of anion structure on the polymerization of Deep Eutectic mixture derived from methacrylic acid and tetrabutylammonium salts

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Deep Eutectic Solvents (DES) are a family of ionic-like fluids with characteristic feature abnormally deep melting point depression for the eutectic composition of certain hydrogen bond donors (HBD) and acceptors (HBA) [1]. DESs are presented as an alternative to ionic liquids thus gaining interest in polymeric materials synthesis [2].

An example of the impact of DES on course of the free radical polymerization (FRP) is polymerization of itaconic acid (IA) in form of DES monomer, which lead to unexpected high molecular weights polymers [3]. In addition, it has been shown that copolymerization of itaconic acid-choline chloride DES monomer is faster than in water [4]. It was also demonstrated that acrylic or methacrylic acid in the mixture with quaternary ammonium salts were successfully polymerized by 'frontal free-radical polymerization' [5, 6].

Course of the FRP in DES depends, among other things on chemical structure of cation and anion in HBA. Little information can be found about influence of the anion in quaternary ammonium salts on FRP of unsaturated carboxylic acid.

In our research we examined the impact of anion in quaternary ammonium salts on photopolymerization of methacrylic acid (MAA). Four ammonium salts with different anions and the same cation (tetrabutylammonium chloride, tetrabutylammonium bisulfate, tetrabutylammonium nitrite and tetrabutylammonium tetrafluoroborate) forming DES with MAA were investigated.

As a part of the study we examined physicochemical properties of DES such as NMR, FTIR spectroscopy, changes in density and viscosity for composition with different molar ratio acid to salt. In addition we determined the conversion curves via RT-FTIR experiment in order to determine of changes in the initial rate of polymerization.

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New Economical method for water treatment in rural areas by magnetite nano particles loaded polymeric nanofibers

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Heavy metals such as lead, copper, nickel, chromium (etc.,) are considered to be toxic to our environment. It is widely found in aqueous solutions where pure water is affected due to chemical manufacturing processes in the industry. This study aims at using simple, economic and sustainable alternative technique that is affordable by poor economic societies for water treatment using nanomaterials. This can be achieved by synthesis of polymeric nanofibers supported magnetite Fe3O4 nanoparticles. The beneficial properties of magnetite in removing heavy metals, adsorption capacity, enhanced catalytic activity, and high dispersion degree and superparamagnetic behavior are reported. Moreover to increase the adsorption by loading the magnetite on porous system in our case, polymeric nanofibers. The magnetite Fe3O4 nanoparticles were prepared using the co-precipitation method to obtain nanoparticle solution. Part of the solution was then put to dry at temperature of 70 ^{o}C for a certain period of time, until a dried magnetite nanoparticles are produced. Nanoparticles are then crushed to reach a fine particle form. A polymer solution was then prepared where a specified concentration of polystyrene (1 gram) intetrahydrofuran (20 milliliters) are stirred together to obtain a polymeric solution. One milligram of magnetite nanoparticles is then added to the solution. The polymer solution with the magnetite nanoparticles was then put into a syringe in order to be applied into a flow rate syringe pump, while connecting a supply voltage to the syringe and a collector, electrospinning process took place. Polymeric fibers are produced onto the collector, in this study we used two types of collectors, the stationary plate collector and the rotating drum collector. Aluminum foil is considered to be the flat plate collector.However, when using the rotating drum collector, aluminum rod was used as the rotating element driven by the motor, while a horizontal flow rate pump is used. Our second approach was to disperse the polymeric nanofibers after the electrospinning process into the magnetite solution to be coated with it. For analyzing the properties of the magnetite nanoparticles and the polymeric nanofibers, spectrophotometer test (UV test) took place to identify the absorbance of the nanoparticles at different ranges of wave lengths, scanning electron microscopy (SEM) was used to identify the grain size, fiber length, diameter size and thenanoparticles distribution in polymeric nanofibers.

Poster Session III

Tuesday, September 28th

Development of hyaluronic acid hydrogels at physiological conditions

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Hyaluronic acid (HA)is a non-sulfated glycosaminoglycannaturallyoccurring in the body,found in connective tissues, skin and synovial joint fluids among others. The polymer chainsare negatively charged at physiological conditions. The hydrophilicity along with their chain conformation and high molecular weight enable to retain high water content. Hyaluronic acid play a vital role as a part of the extracellular matrix (ECM)participating in multiples functions such as cell signal, wound repairing or matrix organization among others [1, 2].HA can be modified and crosslinked to form hydrogels while retain the biocompatibility that characterize the native HA. The hydrogel formation can improvethe physicochemical properties, tunethe time residencein the human body and add new functionalities [3]. In this work, we modify HA introducing thiols groups into the backboneaccording to a method reported elsewhere [4]. Then, the thiolated-HA (HA-SH) is crosslinked withPoly(ethylene glycol) diacrylate (PEGDA) toform hydrogels [5].

Nuclear Magnetic Resonance Spectroscopy (NMR) and Ultraviolet-visible spectroscopy (UV-Vis) were used to assess the substitution degree of thiol groups in the HA. Test tube inverting method was employed to evaluate the hydrogel formation. Hydrogel properties was characterized by rheological characterization.

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Dual role of thioxanthone derivatives for visible light-driven processes

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Thioxanthone-based compounds in combination with hydrogen donor e.g. amine are described in the literature and have been widely used photoinitiators for free radical polymerization, and less frequently for cationic polymerizations [1].

Novel thioxanthone-based compounds were synthesized by palladium-catalysed cross coupling (Suzuki Coupling) reaction and evaluated as a component of photoredox catalysts/photoinitiating systems for the free-radical polymerisation (FRP) of acrylates and the ring-opening cationic polymerisation (CP) of epoxy monomers. Thioxanthone derivativeswith 4-(diphenylamine)phenyl substituent and carbazole-based substituents in position 7 of 2,4-diethylthioxanthen-9-one were investigated and proposed as:

(i) Photosensitizers in bimolecular photoinitiating systems with iodonium or sulphonium salt for cationic polymerization;
(ii) Photosensitizers in bimolecular photoinitiating systems with iodonium or sulphonium saltfor free-radical polymerization;
(iii) One-component free-radical photoinitiators for polymerization of acrylate monomer;
(iv) Type II photoinitiatorsin combination with amines, for polymerization of acrylate monomer.

Performance of the obtained thioxanthone derivatives was investigated in two- and three-component photoinitiatingsystems for photopolymerization processes upon exposure to light emitting diodes (LEDs) with a maximum emission of 405 nm and 420 nm. Fourier transform real-time infrared spectroscopy was used to monitor the kinetics of disappearance of the functional groups of the monomers during photoinitiated polymerization. The influence of thioxanthone skeleton substitution on photoinitiatingeffciency was also studied and discussed.

Furthermore, photoinitiating systems based on novel thioxanthone derivatives was utilized in a stereolithography three-dimensional (3D) printing technology under visible sources of light. The outcome ofthis research is the development of high-performance visible photosensitive resins with improvedphotosensitivity obtained thanks to the development of entirely novel photoinitiating systemsspecifically adapted for this application [2].

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Star polymers nanolayers with antibacterial properties

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Recently, surfaces with covalently grafted cationic polymers have become the subject of intensive research [1]. These polymeric nanolayers are used as, for example, coatings, tissue engineering materials, antibacterial and/or antifungal surfaces. The effect of the modification of the star copolymernanolayers on their antibacterial activity was the main objective of thesestudies. Star copolymers made of N,N'-dimethylaminoethyl methacrylate (DMAEMA) and hydroxyl-bearing oligo(ethylene glycol)methacrylate (OEGMA-OH) were obtained by atom transfer radical polymerization (ATRP). Next, the stars were covalently attached to a solid substratethrough the reaction of OH groups in the arms of DMAEMA with solid support modified with1,1-carbonyldiimidazole. To enhance antibacterial activity of the obtained star nanolayers, the amine groups in the star arms were quaternized or silver nanoparticles (AgNPs) were introduced to the layers by "*in situ*" reduction of the silver nitrate by these amine groups. The obtained layers, before and after the modifications, were characterized by atomic force microscopy (AFM), ellipsometry, quartz crystal microbalance (QCM-D), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The antibacterial activity of star polymer layers with AgNPs, quaternized and nonquaternized against selected bacterial strains was tested and compared.

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Neurologically active drug delivery system based on pyrrole

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Destruction of the central and peripheral nervous system is a serious problem that prevents the proper function of the body. In the elderly age, the incidence of neurodegenerative diseases that damage neurons in the human brain increases. To increase the effectiveness of treatment Alzheimer's disease and the regeneration of damaged nerves, the research involved a synthesis of a polymer film by electrochemical polymerization, taking into account various synthetic protocols and manipulating process parameters to obtain drug delivery systems as a cure that can regenerate damaged neurons [1].

In the research, the pyrrole was synthesized with heparin and the drug substance, which is a phenothiazine derivative in the presence of sodium dodecyl sulfate on a steel substrate. Films were produced on a steel substrate to be applied to a human body.The phenothiazine derivative is used in the treatment of neurodegenerative diseases by increasing muscle motor activity [2]. Layers with embedded drug substance molecules will undergo various characteristics. Cyclic voltammetry will determine the process efficiency, stabilization of the obtained layers, which allowed to determine their quality. Spectroscopic methods such as FTIR determined the composition and behavior of the layers, UV-Vis illustrated the release of medicinal substances. Image analysis using the SEM technique allowedto study the morphology of samples. AFM was used to characterize the roughness of the samples. Hence, the goal of the project is the preparation and characterization of electroactive conductive polymer systems containing embedded different types of drug substance molecules in terms of use in dosing systems used to treat Alzheimer's disease and regeneration of nerves.

As a result of the project, films with embedded drug substance molecules were obtained, showing the possibility of dosing them in the treatment of neurodegenerative diseases (destruction of the central nervous system). Such a designed dosing system will enable the patient to reduce the frequency of taking medications, thus reducing the hospitalization time while increasing the effectiveness of the operation. As well, regeneration of damaged nerves in a human body can improve the healing process.

Keywords: drug delivery system, conducting polymers, polypyrrole, phenothiazines, neurodegenerative diseases

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Amphiphilic hyperbranched polyglycidol as a potential matrix for drug delivery

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Nowadays there is a great interest in polymeric matrixes for drug delivery, especially worth mentioning are amphiphilic polymers. As in their structure it can be differed hydrophobic and hydrophilic segments, they potentially may be used as drug delivery systems [1].

Hyperbranched polyglycidol (HbPGL) exhibits properties characteristic for both dendrimers and polymeric micelles, simultaneously does not require multistep synthesis and purification [2] and what is even more crucial it shows, as well as poly(ethylene glycol), biocompatibility [3], which make HbPGL a great candidate for drug delivery system.

Hydrophobization of the core of HbPGL is possible only if the diol moieties in the shell are protected. As a result of selective and reversible protection of those groups, during modification only the monohydroxyl groups in the HbPGL core can be reacted. After the reaction, process of removing the protection of diol groups of HbPGL is held and as a result amphiphilic polymer is obtained, which have potential as a system of delivery of hydrophobic drugs.

The presentation will be focused on the hydrophobization routes of the inner part of HbPGL. In addition the preliminary results of encapsulation of a model drug will be demonstrated.

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A comparative study on structure and interaction properties ofglycolyzed dendrimers and pseudodendrimers

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Dendritic and Pseudo-dendritic [4] structures have a novel type of density distribution and high number of functional groups, making them quite attractive for medical or biological applications. In the present work, three generations of dendritic and pseudo-dendritic structures have been obtained from hyperbranched aliphatic polyester core by modification of a protected AB^*_2 monomer. The chosen sequence of repeated protection and deprotection steps gave the corresponding dendrimers and pseudo-dendrimers with OH-terminal units. Further modification of all the four generations of dendrimers and pseudo-dendrimers with α-D-Mannose-pentaacetate were performed using copper catalysed "click" reaction, forming glyco-dendrimers and glyco-pseudodendrimers. ^{1}H-NMR was used to confirm the degree of branching and the extent of modification in all four generations. The molar mass of each generation was measured by size-exclusion chromatography coupled to static light scattering. Furthermore, the interaction of glyco-pseudodendrimers with amyloid beta 1-40 is investigated using AF4, ThT assay and AFM. A comparative study of their behavior is performed that gives a concise review of their physico-chemical properties and their possible use in various areas of research. [1-3] Further studies of these dendritic and pseudo-dendritic structures with the amyloid protein residues gives a chance for pioneering investigations in a biological system.

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A Series of Trehalose-Releasing Polymersas Potential Drug Delivery Agents for Autophagy Stimulation

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Autophagy dysfunction is a common cause of various humandiseases, such as neurodegenerative diseases, atherosclerosis, and fatty liver diseases. The activation of autophagy can promote cells regeneration and maintain cellular homeostasis. Currently, trehalose has been widely studied in preclinical trials concerning its chaperone properties and autophagy stimulation. Furthermore, some clinical trials have been conducted to examine trehalose efficacy against autophagy-related diseases. In particular, *in vivo* studies showed thata relatively high oral and intraperitoneal administration of free trehalose is required in order to stimulate autophagy, which might be due to poor drug absorption in the human body. Therefore, there is a need for seeking effective trehalose delivery that can bypass biological barriers and deliver sufficient trehalose to the targeted cells and tissues. In this study, we developed a series of trehalose-releasing polymers that have high colloidal stability at the physiological temperature as tested in different media, includingwater, PBS (pH 7.4), intravenous glucose in saline solution, 4% human serum albumin (HSA) and 10% fetal bovine serum (FBS)-enriched cell media, and primary cell media (low serum). The designed strategy toward trehalose-releasing polymers is based on covalent incorporation of 6-O-acryloyl-trehalose within polymer network, from which trehalose is then released at pH > 7.0 by the cleavage of ester bond which is boosted by 1° and 2° acrylamide-type comonomers. Trehalose-releasing polymers were synthesized via free radical polymerization (FRP) with acrylamide as the main monomer. We successfully fabricated trehalose-rich polymers with high drug conjugation capacity of more than 50%w/w. The loading efficiency and conjugation capacity were assessed enzymatically by measuring the amount of glucose produced after enzymatic degradation of trehalose by trehalase. Interestingly, the increased amount of trehalose feeding (from ~16%w/w to ~64%w/w) in the formulations did not significantly affect the loading efficiency during polymerization. *In vitro* cell study showed that trehalose-rich polymers have low cytotoxicity toward selected human cell lines. In conclusion, the designedtrehalose-rich polymers are a potential candidate for enhancing trehalose delivery and for the treatment of autophagy-related diseases.

Visible light sensitive multicomponent photoinitiator systems for the simultaneous initiation of free-radical, thiol-eneand cationic photopolymerization reactions

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Photoinitiated polymerization is an important process used for a variety of applications, such as photocurable coatings, inks and 3D printing [1].Most of photoinitiators currently used require short-wavelength UV light (below 350nm). UV light sources emitting energy above 350nm adapted in industry are not suitable for these processes because of mismatching between the absorption characteristics of the commercial photoinitiators and the emission characteristics of the light sources [2].

For this reason photoinitiating systems directly adapted to light-emitting diodes (LEDs) as irradiation devices (especially visible LEDs) are designed and developed.1,4-Benzoquinonederivatives were used as a photosensitizers of diaryliodonium salts and triarylsulphoniulm salts for photopolymerization processes. The aim of the work is to study the influence of the structureof the photosensitizers for the efficiency of photosensitization and kinetic of photopolymerization processes.

Fourier transform *real – time* infrared spectroscopy was used to monitor the kinetics of the disappearance of the functional groups of the monomers during photoinitiated cationic, thiol-ene and radical polymerization. Studied 1,4-benzoquinone derivatives have long-wavelength absorption maximum within the range 350 – 500nm Photopolymerization processes were carried out upon irradiation Vis-LED λ_{max}= 405nm or 430 nm and Vis-LED λ_{max}= 450nm.

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Mechanical and structural properties of PVC/halloysite composites

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Poly(vinyl chloride)(PVC) is a thermoplastic material widely used in the industry. It is characterized by good resistance to atmospheric and chemical factors and a low production cost. However, its low thermal stability limit the range of applications of this material [1, 2]. Halloysite(HNT) is a natural clay mineral with many potentially applications in different industrial fields.Due to its unique structure, halloysite has proven to be a filler used to improve the mechanical properties ofpolymer composites, including composites with PVC matrix [3-6].The favorable properties of polymer composites with halloysite related to improvedinterface interaction polymer- filler are in many cases related to the modification of the mineral, including the calcination method [7-9].

Composites based on unplasticized PVC dry blend with raw halloysite from the Dunino mine in Poland and, separately, with calcined halloysitewere prepared in a molten state by using Brabender mixing chamber.The structure of halloysite and PVC composites with 1wt%, 5wt% and 10 wt%of fillers was characterized by SEM observations.Theboth types of halloysite i.e. before and after thermal treatment, were characterized by a plate-like structure with few places where nanotubes were inserted. Based on BET analysis, the size of the specific surface and pores of the mineral is determined. Calcination contributed to the reduction of the specific surface but at the same time, an increase in pore volume is observed.

The SEM imagesof fracture surface of PVC/HNT composites show a homogeneous distribution of the filler in the polymer matrix.The mechanical propertiessuch as tensile strength and Young's modulus were also tested. It was observed that the fracture mode changes from brittle to ductile in the case of the PVC samples containing the calcined mineral in comparison to those containing the non-calcined HNT. The research results indicate an increase in the modulus of PVC/HNT composites compared to unfilled PVC whereby this improvement is more noticeable in the case of calcined halloysite.

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Smart materials based on ethylene 1-octene thermoplastic elastomers TPEand ethylene-propylene-diene rubber EPDM with thermally induced shape memory effect

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Interest in the subject of smart materials has increased significantly in the last few years. They have the ability to react to various stimuli, such as temperature, electrical impulse, heat [1].Polymers with a thermal shape memory effect have found many applications in various industries as well as medicine. These are, for example: textiles, heat-shrinkable tapes, pipe joints, cable sheaths, dental stents and surgical threads [1, 2].

The aim of the work was to obtain smart materials with thermal shape memory using TPE thermoplastic elastomers of the ethylene 1-octene type and EPDM ethylene-propylene-diene rubber, as well as a waste material containing carbon black. The used thermoplastic elastomers responsible for the "hard segment" of the blend were characterized by a different flow index, as well as the content of the crystalline phase. The ground carbon black waste material was used to make a TPE / waste material blend to strengthen the TPE matrix. The morphology of the obtained TPE blends/waste material, mechanical and viscoelastic properties of TPE systems / waste material, TPE/EPDM were examined. The type of thermoplastic elastomer used, and its basic properties strongly influenced the miscibility of the system and the properties of the blends obtained.

The dynamic properties of the materials were investigated using the advanced Ares G2 rheometer. The type of TPE used influenced the rheological parameters, such as the storage modulus G", loss modulus G', tangentδ. The stress relaxation of the material was also determined.The applied elastomeric waste material increased the value of the conservative modulus in comparison to unfilled thermoplastic elastomers. Depending on the TPE used, the blends differed in hardness, tensile strength and damping properties.The obtained elastomer/waste material blends were characterized by a two-phase morphology - the size of the dispersed phase particles and the degree of homogenization was influenced by the type of TPE thermoplastic elastomer used.

For blends, the following coefficients characteristic for the shape memory were determined: *Shape Fixity (F)* and *Recovery Ratio (RR)* [1]: for unfilled thermoplastic elastomer 8411: F = 98%, RR = 91%, 8452: F = 94%, RR = 88 %, 8180: F = 94%, RR = 61%.

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Influence of Processing Parameters on the Shape-Memory Effect of 3D-Printed Halloysite Nanotube Filled Thermoplastic Polyurethane Nanocomposites

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Additive manufacturing of smart polymers is an emerging field of research because the structures of these materials respond to external stimulus. 3D printing has been employed to print polymers with shape memory properties using Fused Filament Fabrication (FFF) machines. FFF machines are usually fed with expensive and commercially available filament feedstock. In this study, Plastic Free forming (PFF) has been employed as an alternative to common Fused Filament Fabrication (FFF). Plastic free former is fed with readily available standard polymer granulates as used for injection moulding. In this study, standard test specimens made of halloysite Nanotube (HNT) filled thermoplastic polyurethane (TPU) were processed by varying printing parameters to evaluate their impacts on the shape memory behavior of TPUs and its nanocomposites. Processing parameter such as such as infill percentage and raster angle on thermos-mechanical and shape memory behavior have been carried out. The obtained results indicated that, increase of infill percentage tends to increase the elastic modulus and tensile strength significantly and the decrease of print angle increased the elastic modulus. However, increasing the infill percentage decreased the significant impact of change of print angle on elastic modulus. The obtained results showed increase in maximum strain values as the infill percentage is increased except when the sample is printed at 0°. Further, highest infill percentage and lowest printing angle tend to increase the shape fixity and she recovery ratio. The results indicate that plastic free forming is an effective technique for creating next generation 4D materials.

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Two-Way Shape Memory Polymers: Thermomechanical Characterization of Reversible Actuation Under Constant Stress vs Constant Strain

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In recent decades,the study of stimuli-responsive polymers has been an interesting topic of investigation due to their vast applications in several fields such as drug delivery systems[1], nanomedicine [2], biosensing [3], from aerospace engineering [4] tosmart textile development [5] just to name a few. The understanding of the mechanism that governs the actuation of such materials is crucial to provide reliable and easy-programmable polymeric-actuatingcomponents in order to suffice their current demand. The present work aims to contribute on the understanding ofthe thermally-induced two-way shape memory effect (2W-SME) of cross-linked semicrystallinepolymers under load. We carried a thoughtful investigation of the thermo-mechanical properties of chemically cross-linked poly(ε-caprolactone) and its comparative evolution under constant stress and constant strain conditions during melting/crystallization cycling. We observed three well differentiated regions of behavior upon cooling for constantly strained materials: rubbery, semicrystalline, and an unexpected and anomalous intermediate stateassociated with entropic softening of the network prior to the crystallization process. Based on the obtained results, we were able to propose plausible mechanisms for the processes occurring in constantly deformed cross-linked polymers upon their crystallization/melting and quantitatively investigatedthe effects of applied stress, elongation degree and cross-linking density to allow programmable design of reversible actuators [6].

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Colloidal assemblies of core-shell hydrophilic spherical and spheroidal particles

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Assemblies of spherical polymer particles are already well known and have been used as elements of optoelectronic devices, nanolithography reagents, and parts of biosensors. Knowledge on formation of setups composed of particles with shape anisotropy, and their properties compared to spherical particles are very scarce.

The aim of these studies was preparation of the spherical and spheroidal hydrophilic core-shell polymer particles and formation of their multidimensional assemblies. The spheroidal particles containing polyglycidol in the interfacial layer (P(S/PGL)) were prepared from the spherical ones. The hydrophilic P(S/PGL) microspheres (with D_n=408 nm) were synthesized by emulsion copolymerization of styrene and polyglycidol macromonomer, using potassium persulfate as an initiator. To prepare spheroidal particles the microspheres were embedded in poly(vinyl alcohol) (PVA) film. The 1 cm -wide stripes of the film containing particles (with conc. ca. 5 wt%) were uniaxially slowly stretched at 120 °C (i.e. above T_g of polystyrene and PVA) to the required length. Finally, the spheroidal particles were isolated by dissolving the film and purified by multiple centrifugation, and resuspended in fresh portions of water. The particles were characterized by SEM, DLS, EA. Composition of their interfacial layer and electric charge deriving from initiator were determined by XPS and measurements of electrophoretic mobility, respectively. From the relation between the film elongation and particles aspect ratio (AR) it was found that AR increased in direct proportion to elongation for AR in the range 1-8. The microspheres' and spheroids' assemblies (see Fig.1) were prepared on silicon supports from particles suspension in water containing EtOH in the concentration range 0-30 vol%. The results of 3D assemblies studies revealed that morphology the assemblies, their optical and mechanical properties depend on particle aspect ratio and on concentration of ethanol in particles suspension.

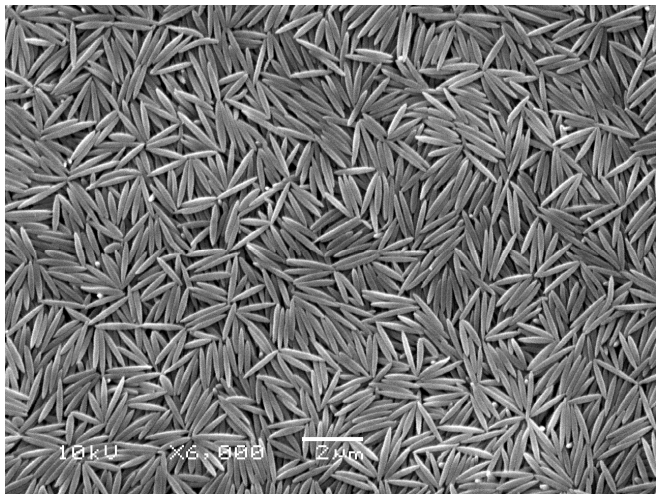

Figure 1. Assembly of spheroidal poly(styrene/polyglycidol) particles with AR=6,41.

Enhanced interactions between PE fibers and cement matrix by applying catechol chemistry

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Reinforcing cementitious matrices with polymeric fibers is a well-accepted approach to attain a controlled crack propagation, higher energy absorption capacity and tensile strength [1, 2]. However, to optimize reinforcing effect a tailored interaction between the fibers and thematrixis needed [3]. While exhibiting unique mechanical properties, high-performance polyethylene (PE) fibers yield low interactions with the water-based cementitious matricesdue to thehydrophobic properties of the polyolefinic constitution [4].An application of catechol chemistry seems to be an effective way to functionalize the PE fibers by forming amino and hydroxyl groups on their surface for improving their wettability and fiber-matrix interactions [5]. In particular, dopamine self-polymerized under a mild alkaline condition can be considered as one of the catechol-based functionalization routes regardless thesubstrate type [6, 7].

In the study at hand, micro-sized PEfiberswere coated with a polydopamine (PDA) layer at room temperature by means of self-polymerization. X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis (TGA), zeta-potential measurements as well asScanning electron microscopy (SEM) confirmed a successful deposition of PDA onto the fibers' surfaces. Forthe optimized reaction conditions,significantly improved fiber-matrix interactions could be proved by single fiber pullout tests. Compared to the unmodified fiber, the interfacial shear strength was enhanced by approximately 90% and the pullout energy by about 300%. This could beexplained mainly by the formation of active hydrophilic groups on the surface, which may react with the cement hydrates acting as docking points, similar to the strong bonded and frequently reported PVA fibers [5, 8].

Overall, use of catechol chemistry can be considered as an effective modification approach for functionalization a variety of fibers for a tailored fiber-matrix interactions and exploitation of full advantages of polymeric fibers in cementitious composites.

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Polymer composites filled with silver nanowires and their properties

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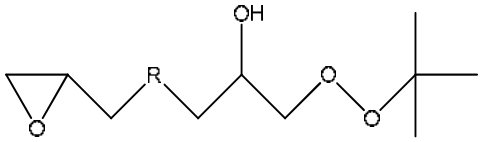
Polymer composites based on silver nanowires (AgNW), due to their unique properties (including optical and conductive), are currently very popular. Nevertheless, AgNW nanocomposites based on basic rubbers (such as styrene-butadiene rubber, or SBR, acrylonitrile-butadiene rubber, or NBR, or carboxylated acrylonitrile-butadiene rubber, or XNBR) are not in the focus of scientists. The work carried out under this topic focuses on the creation of both layered and bulk composites of silver nanowires in order to use them as a conductive medium or mechanical stress sensors. The work includes both the development of composites and the modification of rubbers (used as a substrate) and latex (used as protection of AgNW).

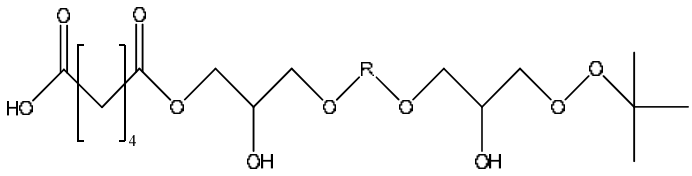
Two resins were used to modify rubbers: monoperoxy derivative of diglycidyl ether Bisphenol A (PO) and carboxylatedperoxy derivative of diglycidyl ether Bisphenol A (CPO), as well as two polymers: polyvinylpyrrolidone (PVP) and polydopamine (PDA). Each of these modifications was aimed at improving the adhesion of silver nanowires to the polymer matrix and changing the mechanical properties of the matrix (for future applications). Both of these goals have been achieved.

Latexes (XSBR, NBR, XNBR) were modified with layered aluminosilicates (talc, mica, kaolin, chalk and montmorillonite) in order to "shorten" and thicken them, so that they could be applied with more methods than the two most suitable for pure latex (which are pouring and spraying). From among the mixtures obtained this way, the ones with a lower degree of filling are used for the application of the Meyer bar method, and those with a high degree of filling – by the screen-printing method. Both unmodified and modified latexes have properties that protect the finished sensor. However, they differ in their mechanical properties, consistency, and the microstructure of the coating.



R = -OC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$O-

Fig. 1. Monoperoxy derivative of diglycidyl ether Bisphenol A (PO)



R = -C$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_4$-

Fig. 2. Carboxylatedperoxy derivative of diglycidyl ether Bisphenol A (CPO)

Colloidal gelation of oppositely charged latexes based on poly(1H,1H,5H-octafluoropentyl methacrylate), polystyrene and poly(ethylmetacrylate)

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Extrusion 3D-printing of functional polymers is technology for making subjects with complicated forms and unique properties [1]. Fluorinated polymersare of great interest due to their mechanical properties, great hydrophobicity, specific optical properties and others.However, low compatibility with aliphatic or aromatic polymers make limited their application [2]. Thus, the development of new methods for combining in one material fluorinated polymers with other materials is perspective topic.In this study we propose creating of colloidal shear-thinning gels based on oppositely charged polymer latexesas an original way for obtaininginks for 3D printing of fluorocontaing materials.

Different latexes based on 1H,1H,5H-octafluoropentyl methacrylate, polystyrene and poly(ethyl metacrylate) was prepared by emulsion polymerization (Fig. 1a) [3].

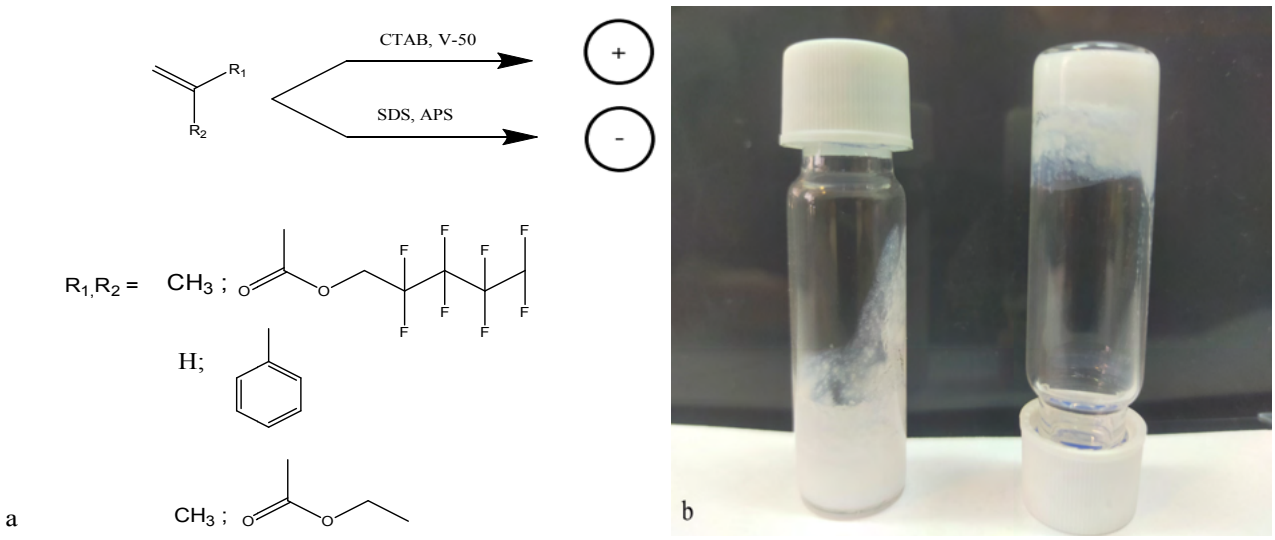

Figure 1:a – scheme for the production of polymer nanoparticles. b – A gel formed from600 µl 10 wt% EtMa+ and 120 µl 7 wt% Flu- NP's at 20 °C.

Charge and size of latex nanoparticles (NPs) was controlled by adding respective initiator and surfactant: 2-2-azo-bis(2-methylpropionamidine) dihydrochloride (V-50) and hexadecyltrimethylammonium bromide (CTAB)for positively charged NPs and ammonium persulfate (APS) and sodium dodecyl sulfate (SDS)for negatively charged NPs.It was shown that negatively charged fluorinated latex forms gels with positively charged ethyl methacrylate latex (fig. 1b). Shear-thinning behaviour of obtained colloidal gels was confirmed by rheological measurents.We propose that regulation of mechanical and optical properties, hydrophobicity and surface morphology of dried extruded gels could be achieved by variation of concentration of fluorinated latexes in the system.

Acknowledgement: This work was supported by Russian Science Foundation (Project No 21-79-20113).

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Synthesis of thermoresponsive nanoparticles based on copolymers of oligoethylene glycol methacrylate containing degradable oligoesterunits

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Thermoresponsive polymers and materials obtained from them,undergo a sudden and reversible change of properties under the influence of temperature.Upon heating, hydrogen bondsbetween polymer and water weakens and intermolecular interactions are dominant, which affects the polymer solubility.The temperature at which phase separation takes place is called cloud point temperature (T_{cp})[1].(Co)polymers of oligoethylene glycol (meth)acrylatesare one of examples of thermoresponsive polymers. They are biocompatible, non-toxic and depending on the copolymer composition, concentration andpresence of additives, they exhibit T_{cp}in a broad region, also at physiological conditions. They have a great potential to be used in medicine, including the intelligent drug delivery systems [2].

In this work copolymers consisting of tri(ethylene glycol) monoethyl ether methacrylate (TEGMA-EE),oligo(ethylene glycol) methacrylate ($OEGMA_{300}$, M_n=300 g/mol), and hydroxyoligo(ethylene glycol) methylether methacrylate (HOEGMA, M_n=360 g/mol)were synthesized by atom transfer radical polymerization[Fig.1]. A degradable oligolactidefragment has been inserted into the polymer chain by ring-opening polymerization. Afterwards, a double bond was introduced into the polymer chain.Copolymers with molar mass of 40000 g/molhave been obtained.The resulting copolymers exhibited a T_{cp}in a range from30^{o}Cto 50^{o}Cin aqueous and saline solutions. $T_{cp}$of obtained copolymers may be controlled by the length and quantity of the oligolactidechain and presence of a double bond [Fig.2a].In dilute aqueous solution, above $T_{cp}$the obtained polymethacrylatesformedparticleswith hydrodynamic diameters from 100nm to 800nm depending onheating procedure and the presence of salt [Fig. 2b]. The double bonds present in the copolymers will be used in the future tostabilize theformed nanoparticles.

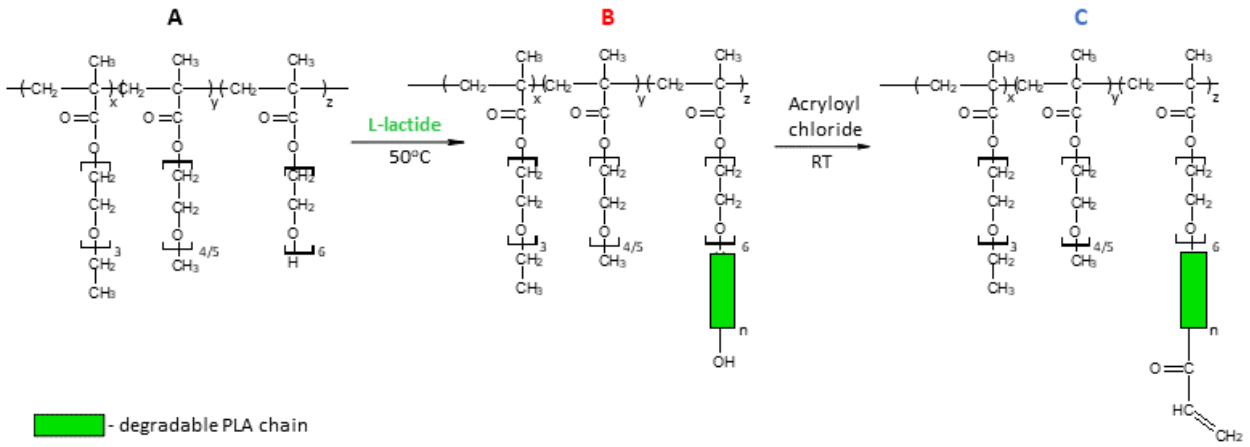

Figure 1: The scheme of copolymer synthesis.

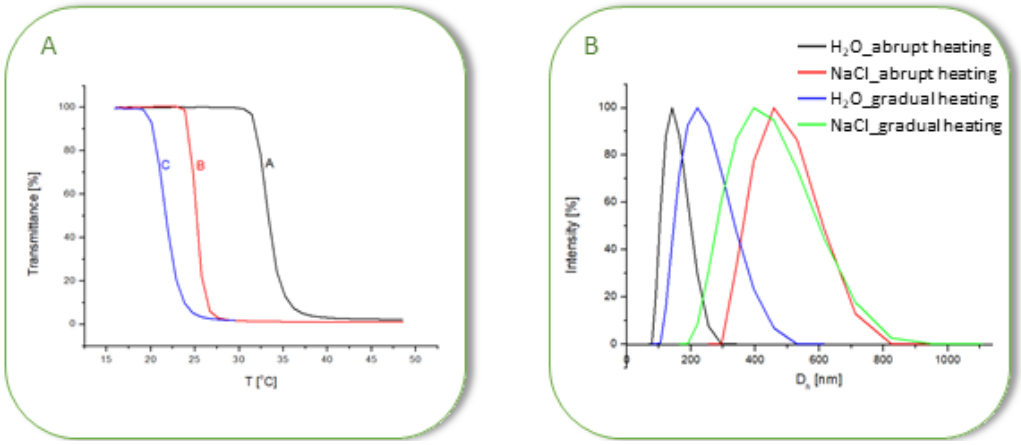

Figure 2: A) Plots of transmittance as a function of temperature (500nm, 1 °C min-1) measured for aqueous solutions (1 mg mL-1) of oligo(ethylene glycol) methacrylates and their derivatives; B) Particle size distributions formed by copolymers of oligo(ethylene glycol) methacrylates containing degradable lactide units, in various conditions (for sample C).

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Thermally-Responsive Hydrogel Materials for Biomedical Applications

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Stimuli-responsive hydrogels have agreat interestfor biomedical applications such as implants, sutures, lenses, catheter, drug transfer scaffolds, etc. due to their physicomechanical properties with the properties of biological tissues [1]. Moreover, by varying their rheological parameters, it is possible to make them suitable for extrusion 3D printing, which will allow achieving micro- and nanostructuring of the materials and expand the range of their functionality.

In this work we focused on two well-known thermally-responsive polymers: gelatin methacrylate (GelMA) with Sol-Gel transition 13-16^{o}C and poly(N-isopropylacrylamide) (pNIPAM) with lower critical solutiontemperature (LCST) 32^{o}C. The first part of the work was related withthe formation of GelMA membranes with different degrees of cross-linking for imitation of blood-brain barrier (BBB). The second part of the work was devoted to obtaining3D printed pNIPAM based materials which will respond differently to several stimuli (magnetic field, temperature, swelling) and can be used in biomedicine and soft robotics as implants and biocompatible manipulators.

Two samples of GelMA with different degree of crosslinking (1-hydroxyclohexyl phenyl ketone as a photoinitiator) were obtainedby controlled photopolymerization: i) GelMA-1 with 0.1 wt% of photoinitiator and UV irradiation for 20 minutes and ii) GelMA-2 0.05 wt% of photoinitiator and UV irradiation for 10 minutes. The resulting membranes were examined for conductivity, porosity, degree of swelling and studied the main characteristics of BBB cells that grew on the resulting membranes - brain microvessel endothelial cells and astrocytes (fig. 1a).

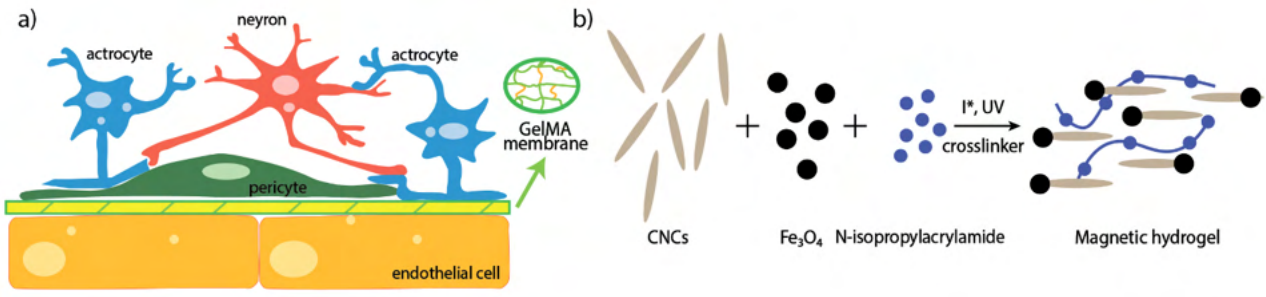

Figure 1. a) Use of gelatin methacrylate membrane to simulate BBB;b) multistimulihydrogel synthesis scheme.

It has been found that the maximally cross-linked GelMA membrane has a more structured fibrillar morphology, higher ionic conductivity, and porosity than the smooth minimally cross-linked membrane. Testing membranes for Lucifer yellow (a known marker of BBB paracellular integrity *in vitro*) permeability showed their perspective for simulating BBB.

Inks for3D printing were obtained by combining cellulose nanocrystals (CNCs), magnetite nanoparticles,N-isopropylacrylamide, poly(ethylene glycol) diacrylate (as a crosslinker)and1-hydroxyclohexyl phenyl ketone (as a photoinitiator)(fig. 1b). The shear-thinning behavior of the resulting ink was confirmed by rheological data: at a shear rate of 0.01 s^{-1} the viscosity was4730 Pa*s, while at shear rate 30 s^{-1}, viscosity was 1.7 Pa*s. The influence of 3D printing parameters on the shear-induced alignment of the anisotropic CNCs was studied.

In further investigations we are planning to combine both strategies for using GelMA and pNIPAM based hydrogels for 3D printing structurally anisotropic stimuli responsive membranes.

Acknowledgements: This work was supported by the Russian Science Foundation (project №21-79-20113).

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Multi-responsive transitions of PDMAEMA brushes for switchable surfaces

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Due to its multi-responsive behavior upon variation of temperature, pH value and ionic strength, poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) is an attractive candidate for switchable surface coatings, especially in the field of biomedical sensors.Using an efficient grafting-to approach, we prepared nanoscopic PDMAEMA brushes grafted homogenously on silicon substrates. These layers were monitored in-situ by an elaborate set of analytical techniques, such as in-situ spectroscopic ellipsometry, in-situ ATR-FTIR spectroscopy as well as in-situ AFM. While PDMAEMA brushes exhibit a lower critical solution temperature (LCST) in aqueous media in the presence of monovalent counterions, it can easily be switched towards an upper critical solution temperature (UCST)thermoresponsiveness via the addition of small quantities of multivalent ions, such as $[Fe(CN)_6]^{3-}$.In-situ FTIR spectroscopy suggests, that the temperature-dependent electrostatic interactions between the polycationic PDMAEMA and the multivalent anions play a crucial role in the unusual UCST behavior of the brushes. Moreover, in-situ AFM reveals the formation of a nanostructured surface of pinned PDMAEMA micelles with entrapped counterions during the UCST transition, whereas a homogenous brush surface was detected both below and above the LCST. Furthermore, transition temperatures as well as the sharpness of the thermoresponse were successfully tuned via secondary triggers, like changes of the pH-value or the ionic strength. Multi-responsive PDMAEMA brushes therefore provide an excellent platform to tailorsurface properties under aqueous conditions,paving the way towards smart coatings for catalysis, drug delivery or sensing.

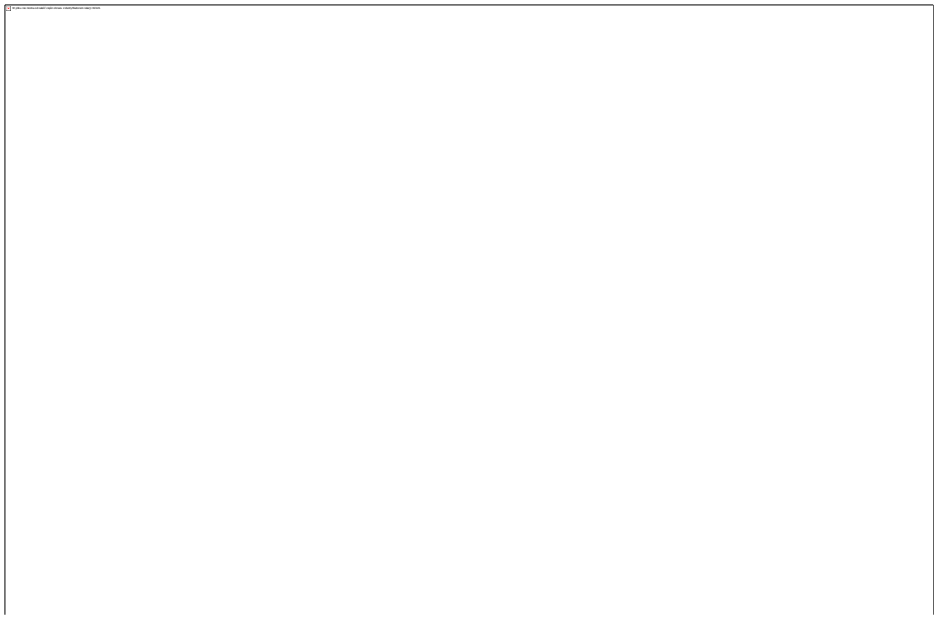

Figure 1: In-situ characterization of the thermoresponsive transitions of PDMAEMA brushes under aqueous conditions.

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Microstructural analysis of stimuli responsive polymersomes in targeted delivery of active substances

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The engineering of stimuli-responsive polymersomes for application as artificial organelles and nanoreactors has revolutionized biomimetics [1]. We present the first-time utility of pH-sensitive and crosslinked polymersomes fabricated from poly(ethylene glycol)-*b*-(poly(diethylaminoethyl methacrylate)-*s*-poly(dimethylaminoethyl methacrylate)-*s*-poly(dimethylmaleimidobutyl methacrylate)) as artificial organelles for enzyme loading and targeted release. In this study, a post-loading process during the swollen state of the polymersomes was used, in which a reversible change in membrane permeability and size occurs [2, 3]. Moreover, this post-loading process can be modulated by various parameters such as the size of the bio(macro)molecule, the surface charge, the presence of high salt concentrations, etc[4]. By post-loading, different bio(macro)molecules were loaded and subsequently characterized by cryo-TEM, fluorescence spectroscopy, dynamic light scattering, and asymmetric flow field-flow fractionation (AF4) to determine different parameters like shape, size, loading efficiency, and main locations into the polymersomes.

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Methods of devulcanization of recycled rubber from end-of-life tires

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In the present study, the devulcanization and further characterization of recycled rubber from end-of-life tires was carried out by two approaches: (i) selective devulcanization by chemical treatment with thiols applied on natural rubber (NR-S) and to carbon black filled natural rubber samples (NR-S-CB) and (ii) Random devulcanization by thermo-mechanical treatment on end-of-life tire powder (ELTP) and ELTP containing bitumen as an additive (RAR-X), in which, bitumen worked as a facilitator agent for recycling and processability the ELTP.

Devulcanization method i) consisted in the immersion of NR-S and NR-S-CB specimens varying the time of exposure in propanethiol/hexylamine and hexanethiol/hexylamine solutions and their subsequent rinsing in toluene, recovery, and dryingprocesses. For devulcanization method ii) the ELT and RAR-X powders were treated by thermo-mechanical devulcanization using an internal mixer at high temperature and enough time to guarantee the breakage of crosslinks and the main polymeric chains. Subsequently, a sulfur-based vulcanization system was added to the devulcanized powder of ELT to reprocess it and manufacture specimens for further test.

The structural characterization of the natural rubber compounds made it possible to establish the limits of selective devulcanization, allowing correlation with Horickx's theory [1]. This characterization was carried out on all the specimens by experiments of double quantum nuclear magnetic resonance (^{1}HDQ-NMR), from this technique quantitative advanced characterization of the elastomeric network was obtained, as well as the amount ofnetwork defects, entanglements, and crosslink densities [2]. Thus, it was possible to determine the effect of the devulcanization treatment on the samples studied, which was mainly selective for the NR-S specimens and random for the ELT powder due to the different treatments applied on each sample. On the other hand, in the samples of ELTP devulcanized by thermo-mechanical methods it has been determined that they show a lower crosslink density due to the breakage of these junctions and the polymeric chains [3]. In addition, it has been possible to quantify the elastomeric network content: the percentage of polysulfide and disulfide junctions and the amount of defects (extractable part, dangling chain-ends, loops, etc.) thus, establishing the selectivity of these devulcanization methods and the effect of the bitumen on the quality of the composites manufactured.

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Factors Affecting Fiber Morphology in Green Electrospinning

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Electrospinning is a well-stablished technology used to create polymer nanofibers. This technology has gained extraordinary relevance in the last years due to its simplicity, low cost and the possibility toeffectively scale it up to industrial levels. Electrospun nanofibers are very attractive for a broad range of applications such as textiles, filters, tissue engineering, drug delivery, wound healing, sensor, energy storage, catalysis and many more [1-3].

Although Solution Electrospinning is the most widely used electrospinning method, it presents some limitations for industrial applications. The first limitation is the need of toxic and flammable organic solvents. The second limitation is themaximum critical polymer concentration that can be used in the process (around 10-15 wt % of polymer). Polymer solutions of higher concentrations are not spinnable due to their high viscosity. This concentration limitation decreases the productivity of the electrospinning process importantly.Green Electrospinning is a novel and promising method in which fibers can be spun froman aqueous polymer dispersion (latex) with the help of a template polymer. This method overcomes the above mentioned limitation as it allows the use of water as electrospinning medium and enables to spin solutions of higher polymer concentrations increasing the overall productivity of the process [4, 5].

In this work we have electrospun poly(methyl methacrylate-co-butyl acrylate) (PMMA/BA) polymer particles using polyvinyl alcohol (PVA) as template polymer. We have compared samples with different solid content and different PVA/polymer particles ratio with the objective to find the minimum necessary PVA amount in order to obtain uniform and continuous water resistant fibers. Additionally, polymer particles surface functionalized with of carboxylic acid groups have also been electrospun at different pH values in with the objective to study the effect of the particles surface functionalization and pH on the final nanofibers morphology. Finally,the influence of the use of a bimodal particle size distribution on the final nanofiber morphology has also been studied.

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Variable temperature asymmetric flow field-flow fractionation for the topology separation of poly(methyl methacrylate)

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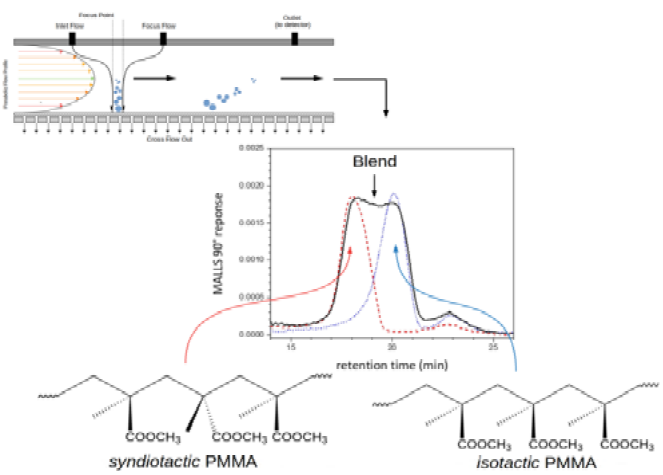
Asymmetric field flow-field fractionation (AF4), a channel-based technique, is considered to be a complementary fractionation technique to size exclusion chromatography (SEC), a column-based technique, for molar mass and molar mass distribution characterization of complex polymers. The separation in SEC governed by the differences in the hydrodynamic sizes the analytesin solution adopts at a specific temperature.As the resolution in SEC is low, the separation ofpolymers with similar degree of polymerization, where the difference in hydrodynamic size is as a result of the difference in chemical composition or molecular topology, can be insufficient.



In the case of AF4,separation is governed by the differences in the diffusion coefficients (D) of the analytes in solution. D is a function of hydrodynamic size, which correlates to the primary molecular parameters such as, chemical composition, degree of polymerization and molecular topology. In addition, the thermodynamic quality of the solvent and the analysis temperature influence the hydrodynamic size of the analytes in solution. Presumably, as AF4 separation is predominantly governed by D, the separation of polymers with difference in tacticity can be achieved by AF4.

To illustrate the separation capabilities of AF4, syndiotactic- (*s*-PMMA), atactic- (*a*-PMMA) and isotactic (*i*-PMMA) poly(methyl methacrylate) of similar molar mass, were analysed.In addition to developing a separation method, the effects of the solvent quality and channel temperature on the separation were investigated. The sensitivity of AF4 was illustrated, as PMMA samples with different tacticity, but similar molar mass, had different retention times within the channel. Additionally, it was concluded that the thermodynamic quality of the carrier liquid can have a significant influence on the retention behaviour of polymers in AF4. It was found that by using chloroform, a non-stereocomplexingsolvent, as carrier liquid, a blend of *s*-PMMA and *i*-PMMA could be analysed. A bimodal peak distribution was obtained for the blend. This very nicely shows the flexibility of AF4 as compared to SEC.

Thermal field-flow fractionation-UVVis spectroscopy: Correlating surface plasmon resonance with size and composition of gold-polymer hybrid nanoparticles

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This study discusses the characterization of microstructure, kinetics, and dynamics of gold-polymer nanoparticle (Au-Polymer NP) hybrids as obtained by thermal field-flow fractionation (ThFFF) hyphenated with UVVis spectroscopy and dynamic light scattering (DLS). This technique represents a novel strategy for correlating surface plasmon resonance (SPR) with information on size, chemical composition, and ThFFF retention behavior of Au-Polymer NPs. Smaller-sized Au-Polymer NP hybrids were produced by increasing the Au content. The decrease in size resulted in higher (1) ThFFF retention, (2) blue-shifts in UVVis, and (3) SPR band intensities. It was found that chemical composition superseded size in governing ThFFF retention. As a demonstration of high detection sensitivity, distinct SPR bands were recorded with ThFFF-UVVis for Au-Polymer NP hybrids that were previously undetectable using batch UVVis spectroscopy. Owing to this hypersensitivity, SPR and its distribution are shown to be superior probes for monitoring trace changes in size (and presumably shape) of Au-Polymer NP hybrids, changes otherwise unresolvable with only light scattering techniques.

Selectively superabsorbent nanoconfined poly(ionic liquid) gels based on poly(N-vinylimidazole) containing conetworks

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Nowadays, ionic liquids (IL) have an important role in chemistry and chemical technologies because the special properties of such materials. Most of the known ionic liquids possess good chemical and thermal stability, high conductivity, and wide electrochemical stability window. Poly(ionic liquids) (PIL), that is polymers containing ionic liquid moieties, have the same behavior like ILs, but their mechanical stability, processability and durability is usually better than their low molecular weight counterparts. PILs as new types of polyelectrolytes are used in various fields, such as gas absorption, separation, electrochemical devices and fuel cells.

New types of nanoconfined poly(ionic liquid) conetworks were synthesized from poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) amphiphilic polymer conetworks by the alkylation of the imidazolium ring in these crosslinked polymer assemblies [1]. The properties of the new crosslinked PILs were investigated with a variety of methods. Solid phase NMR measurements showed that the alkylation was quantitative. The results of the DSC measurements indicated a very special behavior, the glass transition temperatures of the components are very similar to that of the components of the starting APCNs,but the crystallinity of the PTHF phase is decreased in the PIL conetworks. The AFM and SAXS results show that the structure of the PIL conetworksis phase separated, and the average domain sizes are between 10-20 nm, that is the PIL component is confined inside the conetworks in the nanometer ranges. The swelling behaviorof the PILs are very special, they show the amphiphilic properties, on the one hand. On the other hand, surprisingly, it was also found that these new PIL conetworks behave as selective superabsorbents for certain polar organic solvents, such as DMF, DMSO, NMP [1]. These results indicate that the novel nanoconfined PIL conetworks obtained by *in-situ* successful alkylation of the imidazole rings in PVIm-*l*-PTHF conetworks are promising materials for a variety of high value-added unique application possibilities ranging from specialty nanohybrids to electronics, medical and environmental protection purposes.

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The *scissors effect* in nanophasic polymer conetworks: The unprecedented Fox-Flory relationship between the glass transition temperature and M_c of the crosslinked polymer

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Polymer conetworks, composed of different polymers chains crosslinked by chemical bonds, have gained significant interest in recent years. Especially, conetworks with immiscible macromolecular components, such as hydrophilic and hydrophobic polymers, are of special importance, mainly due to their nanophase separated structure. The phase separation has been proved by various techniques, such as DSC, SAXS, SANS, solid state NMR and imaging methods, e.g. AFM and TEM. In case of immiscibility, DSC usually shows two distinct glass transition temperatures (T_g), which is one of the most important properties of polymeric materials. Surprisingly, it was found for poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) amphiphilic polymer conetworks that the T_g of the PVIm components decreases with increasing crosslinking density, i.e. with decreasing average molecular weights between the crosslinking points (M_c), and the T_g as a function of M_c follows the Fox-Flory relationship($T_g = T_{g,\infty} - K/M_c$) which is valid for free-standing homopolymers [1]. This indicates that the macromolecular crosslinkers act like a scissors in relation to the glass transition of the crosslinked polymer. Thus, this phenomenon is termed as the*scissors effect* [1].

In order to reveal whether the *scissors effect*, i.e., the Fox–Flory relationship between T_g and the average molecular weight between crosslinking points (M_c), is more generally effective or valid only for a single case, i.e. for the PVIm-*l*-PTHF amphiphilic polymer conetworks, a series of poly(methyl methacrylate)-*l*-polyisobutylene (PMMA-*l*-PIB) conetworkswith broad composition ranges were synthesized by using methacrylate-telechelicPIBmacrocrosslinkers having a variety of molecular weights. Two T_g*s* were found for all the PMMA-*l*-PIBconetworksby DSC. Fox-Flory type dependence between the T_g and M_c of the PMMA component was observed [2]. The *K* constants for the PMMAhomopolymer and for the PMMA in the conetworksare the same in the margin of error. AFM images indicated disordered bicontinuous, mutually nanoconfined morphology with average domain sizes of 5–20 nm, but the correlation between T_g and domain sizes was not found. These new results indicate that the macrocrosslinkers act like molecular scissors (*scissors effect*), and the T_g of PMMA depends exclusively on the M_c in the conetworks. Consequently, these findings mean that the *scissors effect* is presumably a general phenomenon in nanophase-separated polymer conetworks. This unprecedented finding could be utilized in designing, processing and applications of these novel materials.

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Processing of fast-gelling hydrogel precursors in microfluidics by electrocoalescenceof reactive species

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Microscopic hydrogels also referred to as microgels, find broad application in life and materials science. A well-established technique for fabricating uniform microgels is droplet microfluidics. To yield uniform microgels with respect to their morphology, mechanics, and distribution of functional moieties, optimal mixing of hydrogel precursor components is crucial. However, processing highly reactive polymer precursors is challenging due to the risk of instantaneous, uncontrolled gelation causing microchannel blockage and device failure [1].

We address this challenge by utilizing microflow cells with integrated electrodes, which enable fast addition and mixing of hydrogel network precursors on demand through emulsion coalescence [2]. Here, two populations of surfactant-stabilized aqueous droplets – the first containing the material basis of the microgel and the second containing another gel-forming or crosslinking component are formed at two consecutive microchannel junctions and merged *via* temporary thin-film instability.

Using our approach, hydrogel systems that are otherwise challenging to process into uniform droplets and microgels by conventional droplet microfluidics become processable. To demonstrate its versatility, we fabricate microgels with uniform shape and composition based on fast hydrogelation *via* thiol-Michael addition reaction or *via* non-covalent self-assembly by supramolecular or ionic crosslinking.

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Formulation and characterization of rifampicin-loaded polyanhydride microspheres

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Polyanhydrides are a class of surface-degradable polymers characterized by anhydride bonds in the main chain. They are obtained by polycondensation of compounds containing two carboxylic groups. Polyanhydrides undergo hydrolytic degradation to their respective diacids which are completely eliminated from the body within a short period of time. Due to their properties, such as lack of toxicity and appropriate release kinetics of active substances, they are mainly used in medicine, both as drug carriers and as biomaterials [1].Disuccinatebetulin (DBB) containing two carboxylic groups is excellent raw material to obtain polyanhydrides.Furthermore, both betulin and betulindisuccinate show lack of toxicity in vitro and in vivo [2].Until now, there haven't appeared reports regarding the use of polyanhydrides from betulin derivatives in controlled drug delivery systems.

The aim of this work was preparation and characterization of polymer-drug systems, based on polymeric microspheres obtained from polyanhydrides composed of betulindisuccinate and sebacic acid. The active compound which was coupled to the betulin-based carriers wasa rifampicin, an ansamycin drug, used in the treatment of tuberculosis.Betulin and its derivatives have a broad spectrum of biological relevance, thus these compounds are promising as new, potential therapeutic agents. Microspheres prepared from betulin-based polyanhydrides may have significant application in drug delivery systems.

The microspheres were obtained by emulsion solvent evaporation method from polyanhydrides based on betulin disuccinate and sebacic acid. The content of sebacic acid in the copolymers was 20, 40, 60 and 80 wt%, respectively. The size of themicrospheres was in the range of 1-10 μm (for small particles obtained at 18,000 rpm) or 10-30 μm (for large particles obtained at 3000 rpm).

In the study, 24 polymer-drug systems were obtained, in which rifampicin was used as a biologically active compound. Small and large rifampicin-loaded microspheres were obtained for each of the copolymers. The initial amount of drug was 10, 30 and 50 wt%, based on the weight of the polymer. Parameters such as the actual rifampicincontent in the microspheres, encapsulation efficiency and drug loading weredetermined.The encapsulation efficiency and drug loading were dependent on the polymer composition, particle size and the starting amount of the drug. The highest degree of drug loading was observed for large particles, in which the initial amount of drug (at the particle preparation stage) was 50 wt%. The composition of the polymer from, which the polymer-drug systems were obtained also had a great influence on the degree of drug loading. The least amount of drug was introduced into the microspheres obtained from a copolymer containing 80 wt% of sebacic acid.

In vitro release profiles of rifampicin from tested polymer-drug systems were also determined. Rifampicin is released from microspheres for a relatively long time (about 1 month for most systems). The rate of rifampicin release from the microspheres depends on the degree of drug loading (the more drug loaded, the longer rifampicin is released from the microspheres), and also of the composition of the polyanhydride from which the microspheres were obtained.

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Hydration studies of the synthetic components of articular cartilage

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Osteoarthrosis (OA) is a degenerative joint disease that is characterized by pain and stiffness. It is considered as the most common joint disease that affects humans. Osteoarthrosis can be either genetic, as well as a result of trauma or constant strain on the joints. It is usually diagnosed by physical examination, radiography, computed tomography, magnetic resonance imaging, and arthroscopy. However, the effective diagnosis of early stage of OA is still challenging. Raman spectroscopy has a great potential to fulfil all requirements in this field as it offers full biochemical information about the tested issues [1].

Currently, some various scales of joint degeneration are used, unfortunately, all of them are subjective [2]. Spectroscopic methods (including Raman spectroscopy) after protocol standardization allow for more precise classification of tissue damage. In order to determine precisely the spectral factors which can be useful for OA diagnosis it is important to know what changes accompany a given stage of osteoarthritis. Thus, it is necessary to examine individual components that are included in the cartilage. It has been shown that as the degradation of the friction surfaces in the joint progresses, quantitative changes occur in individual components such as collagen [3].An appropriate intervention that could prevent total joint replacement surgery is the improvement of the tribological properties between joint surfaces. There is great hope in the use of novel bottle-brush copolymers with biocompatible phosphorylcholine methacrylate and cartilage-anchoring blocks that would chemically attach to damaged surfaces reducing the friction coefficient between them. To successfully design and next deliver and anchor the bottle-brush polymers on cartilage surface the deep knowledge on intermolecular interactions in the system are required including hydration of particular chemical components of cartilage.

Collagen forms approximately 70% of the dry weight of adult articular cartilage [4]. Cartilage zones differ in the orientation of collagen fibers. The amino acid composition of collagen is a characteristic feature and consists of 19 amino acids, moreover one of them, namely hydroxyproline, does not occur in other proteins. Glycine, proline, and hydroxyproline make up to more than half of all amino acids in collagen. The triple helix of collagen is made of three chains connected by covalent bonds formed by concentrically arranged glycine. The helical structure is mainly formed by alanine, phenylalanine, tyrosine, asparagine and glutamine. The regular helix structure is disrupted by proline and hydroxyproline, among others. In case of proline, the nitrogen atom is attached to a heterocyclic ring, and the chain can curve or even form loops [5].

In the present study, four components of non-animal origin, which are among the main components of collagen, were selected. L-alanine, L-proline, hydroxyproline and glycine in powder form were used for investigation. Using Raman and FTIR spectroscopy, the substances were examined in dry form, in the form of solutions in milli-Q water and in the form of solutions in 0.9% saline, which mimic a physiological fluid.

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Novel safe amine-free initiating systems for the preparation of photo-cured dental materials

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Photopolymerization processes play an essential role in various fields such as coating industry, automotive, photo-curing, 3D printing. More and more often, photopolymerization processes are also used in biological applications. Especially in recent years, the trend of obtaining dental fillings by means of photopolymerization has increased. The use of photochemically initiated polymerization to obtain dental composites enables the use of unique and innovative features of this method. The most important are: (a) short curing time of the composition (up to a few seconds), (b) carrying out the reaction at room temperature, and (c) low energy consumption [1].

The most common initiating system for the preparation of photocurable dental composites is the system composed of camphorquinone and aromatic amine, especially ethyl 4-dimethylaminobenzoate (EDB). Nevertheless, camphorquinone generates a yellow colour, while amines are cytotoxic and genotoxic. The most popular materials designated for obtaining dental composites through photopolymerization are (meth) acrylate monomers (RCB - resin-based composites) characterized by high reactivity, which form an organic matrix. Nevertheless, acrylate monomers cause high polymerization shrinkage. Polymerization shrinkage in composite materials can lead to the formation of a marginal gap between the photo-cured filling and the tooth tissue, leading to micro-leakage. Therefore, new organic matrices as well as initiating systems for the production of photo-cured dental fillings are still being sought [2,3].

In this work, we present entirely new initiating systems for the production of photo-cured dental materials. Besides, completely new organic matrices leading to the formation of an interpenetrating polymer network have been proposed. The influence of inorganic fillers on hardness and conversion rates was also investigated. Dental composites conversion rates were studied using real-time-FT-IR, while hardness was measured on the Shore scale.

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Synthesis of PU-Si-Ti based sol-gel hybrid materials incorporated with Fe_3O_4 nanoparticles for biological applications

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In recent years, research in the biomaterial field has allowed the development of tissue implants with high performances using several classes of materials such as metals, alloys, polymers, glass/ceramics and composite materials [1]. However, currently an implant has a lifetime of just 15-20 years and, thus, young or dynamic recipients often need other operations to replace the failed prosthesis. The implant failure can be due to many causes such as mechanical, chemical, tribological, surgical, manufacturing and biocompatibility problems
[1, 2].

In this sense, Tissue engineering shows great promise in this field.The development of new materials has strongly increased, and an attractive candidate are organic/inorganic hybrid materials: biphasic systems in which the organic and inorganic components are connected on a nanometer scale. Many organic/inorganic hybrid materials can be easily developed using the sol–gel method. The sol-gel chemistry is based on the hydrolysis and polycondensation reactions of the precursor metal alkoxides. Formation of the material takes place in solution at low temperature, allowing introducing easily the organic phases in an inorganic matrix, while preventing its degradation [3].

Furthermore, the addition of Fe_3O_4magnetic nanoparticles provides multifunctionality to materials such as enhanced mechanical properties and due to its magnetic character, cell proliferation and magnetic hyperthermia [4].

In this work, we report the synthesis of hybrid materials from a segmented based Poly(ε-caprolactone) PCL, 1,6-Hexamethylene diisocianate (HDI) and 3-aminopropyl-triethoxysilane (APTES)polyurethane as organic component and titanium (IV) butoxide and APTES as inorganic component, in a 50:50 ratio. Finally, Fe_3O_4 nanoparticles previously characterized by DLS, Z Potential and TEM were added to materials in 0.5, 1.0 and 2.0 W%.Their chemical structure were characterized by FTIR and solid-state NMR, and corroborated by the study of their mechanical properties. DSC and TGA were performed in order to determinate the thermal behavior and thermal stability. The surface was characterized by contact angle and SEM.

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Magnetically Navigated Polymer Capsules as Nanoreactors Loadable at the Oil/Water Interface

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Magnetic remote navigation and drug targeting toward the intended pathology sites as well as magnetically controlled release of biologically active compounds are the current challenges in the development of smart multifunctional drug delivery systems.Polymer capsules with oil, liquid and magnetic cores in combination with the semipermeable walls would allow us to carry out chemical reactions inside the capsules cores in a cyclic manner. Such reusable polymer nanoreactors possess great potential for carrying out chemical reactions in a controlled and highly efficient way.

The capsules with chitosan-based shells were formed in a one-step process by emulsification of an aqueous solution of the hydrophobically derived chitosan and oilphase containing the dispersed superparamagnetic iron oxide nanoparticles (SPIONs). In this way, magnetic capsules with a diameter of approximately 500–600 nm containing encapsulated SPIONs were formed which was confirmed with the use ofdynamic light scattering and scanning transmission electron microscopy measurements. The water-dispersible capsules, thanks to their magnetic properties, were then navigated in a static magnetic field gradient and transferred between the water and oil phases. Usingsuch an approach, the capsules could be loaded in a controlled way with a hydrophobic reactant, perylene, which was later photooxidized upon transferring the capsules to the aqueous phase.

The capsules were shown to serve as robust reloadable nanoreactors/nanocontainers that, via magnetic navigation, can be transferred between immiscible phases without disruption [1].

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Crosslinked ADMET Polyester as a Novel, Bio-Derived Solid Polymer Electrolyte for Lithium-Ion Conduction

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Solid polymer electrolytes (SPEs) are a promising form of solid-state electrolyte expected to replace traditional liquid electrolytes in the next-generation of lithium-ion batteries [1].When compared to liquid electrolytes, SPEs offer several advantages such as improved electrochemical and mechanical performance, improved safety and lower cost. Moreover, they also offer the advantage of being flexible and transparent when compared to inorganic garnet-type solid-state electrolytes. However, SPEs still currently suffer from lower ionic conductivities at battery operating temperatures. Polyethylene oxide (PEO), and other polyether/polyacetals, have received a lot of attention due to the high ionic conductivity (*c.a.* 10^{-3} S cm^{-1} at 70 °C) above the melting temperature of PEO, although their poor room temperature performance, high crystallinity and low lithium transference numbers (typically around 0.2) remain a limitation to their practical implementation [2].Polyesters and polycarbonates have also been studied as alternative polymer hostsamongst others, as well as more 'exotic' materials such as single-ion conducting polymers [3]. However, in most of these cases, these polymers are derived from petrochemicals and there has been less research concerning the application of bio-derived polymers in SPEs [4].

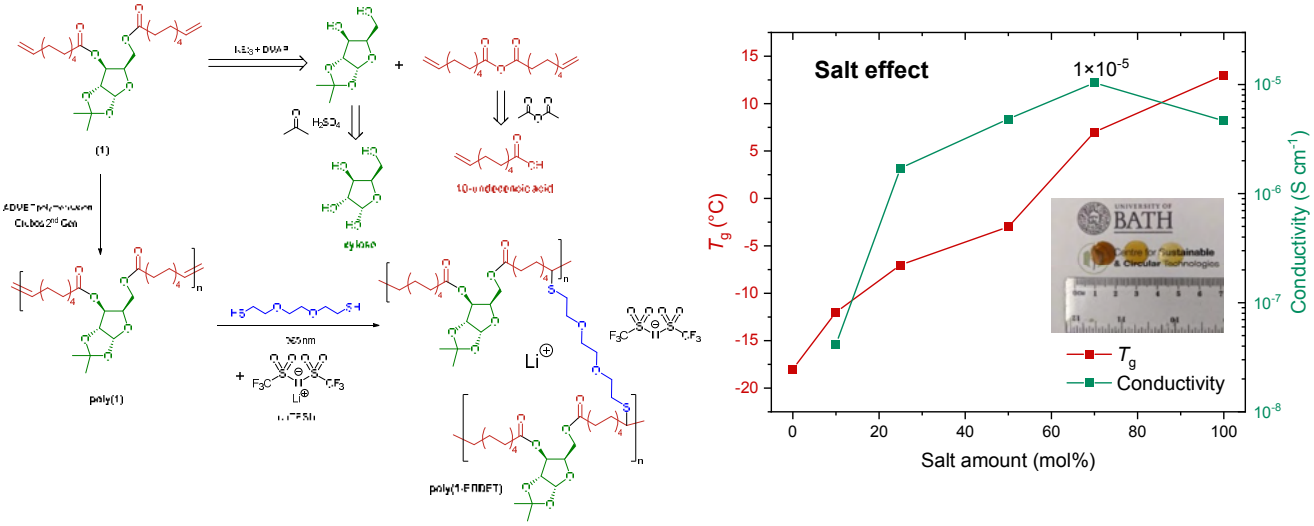

Figure 1. Left: scheme of the synthetic route to crosslinked SPEs derived from xylose and10-undecenoic acid. Right: chart showingthe effect of increasing salt molarity on the glass transition temperature and ionic conductivity of the SPEs (0.05 crosslinker equivalents, $M_{n,SEC}$ = 24.7 kg mol^{-1}) with embedded photo of representative samples.

Herein, we demonstrate the use of a recently reported bio-derived ADMET polyester in SPE applications [5]. The polymer, derived from xylose (a renewable sugar carbohydrate) and 10-undecenoic acid (a castor oil derivative), is crosslinked with a small amount of 2,2'-(ethylenedioxy)diethanethiol (a dithiol resembling PEO) in order to provide mechanical strength to the material. After optimising the molecular weight, crosslinking density and salt molarity of the SPE, an ionic conductivity in the region of 10^{-5} S cm^{-1} has been achieved at 60 °C with a lithium transference number >0.5. We hope that this initial study will pave the way for further investigations of SPEs with this type of material.

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Sulfur containing polymers by inverse vulcanization for high-capacitysolid-state lithium-ionbatteries

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Copolymerization methods, like the inverse vulcanization [1] have gained significant interest in the last decade. Inverse vulcanization,a solvent-free process that enables the synthesis of low-cost materials has great potentials in thefield of Li-sulfur batteries [2].

The amount of the sulfur determines the capacity in the polymer.Our aim was to prepare polymers with increased sulfur content using low molecular weight hydrocarbons (C7). In this research work,a solvent-free process, norbornene as organic componentand sulfur (S_8) wereselected for investigating this possibility. The elemental sulphur is an unvaluablecoproduct and norbornene is also a low-cost product in oil industry [3].

In this presentation,we will focus on theinverse vulcanization processwith norbornene and elemental sulfur, the preparation, characterization (^{1}H and ^{13}C NMR, GPC, etc.) of the novel polymer was also carried out. We have optimized the conditions to increase the yield of the polymer andsuccessfully recirculate the coproducts to achieve the polymers in high yields and purity.

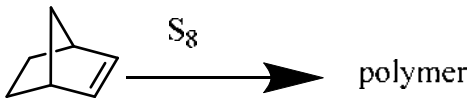

Figure 1. Inverse vulcanization of norbornene.

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Synthesis of high performance supercapacitor electrode materials based on polyaniline and carbons

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Nowadays, the rapid growth of portable electronics and hybrid electric vehicles propels the development of electrochemical capacitors, also known as supercapacitors, to the forefront of research [1]. Current research on electrochemical capacitors aims to increase power and energy density while also lowering fabrication costs by using environmentally friendly materials.Electrochemical capacitors are classified as electrical double-layer capacitors (EDLCs) or pseudocapacitors based on their charge storage mechanism and active material type [2]. Carbon materials with a high specific surface area are commonly used in EDLCs. EDLCs charge and discharge via rapid ion adsorption and desorption [3]. On the other hand, pseudocapacitors are fast and reversibly chargeableby redox reactions of transition metal oxides or conductive [4].

Because of its low cost, ease of production, and relatively high conductivity, polyaniline (PANI) has been regarded as one of the most potential electrode materials [5]. However, similar to other conducting polymers, PANI has a low power density and instability during the electrochemical reactions. Therefore, high PANI dispersion on a support material with good conductivity and a large surface area should be a promising strategy to increase PANI's capacitive capabilities.

In this study, our aim is to produce polymer carbon-based composites with high energy densityand high capacitances for supercapacitor electrode materials. PANI/carbon materials are synthesized by in-situ chemical oxidation polymerization of aniline in presence of different carbon materials.At present, morphological, electrical and electrochemical properties of various prepared materials are examinedin order to select the most appropriate electrode material for preparation of printable, long lasting supercapacitor electrodes. First results will be presented.

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Polymers of intrinsic microporosity (PIMs) for electrochemical energy storage

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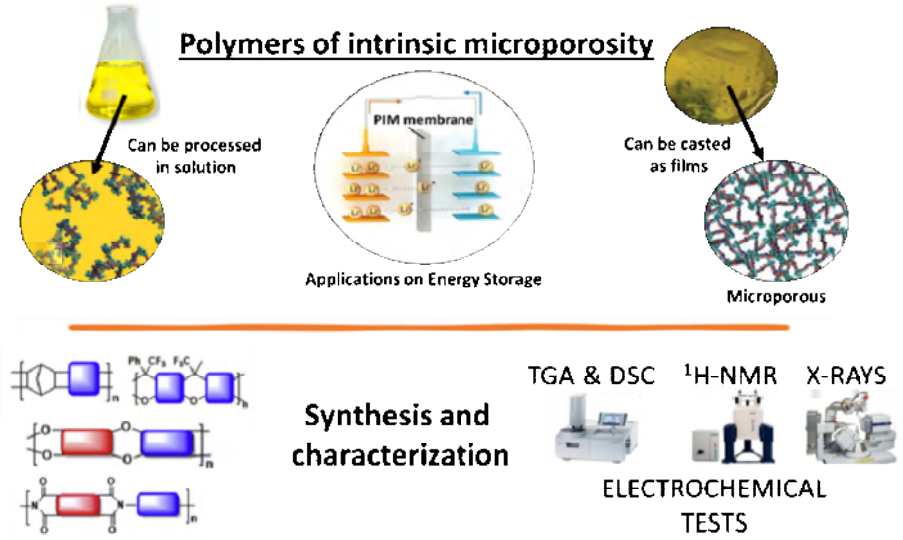
The development of sustainable, permeable and selective electrochemical polymer membranes is of increasing interest since it would allow controlling the ion conduction in several electrochemical processes boosting their application in the field of energy storage.

On the one hand, PIMs aremicroporous materials not covalently crisscrossed that due to their rigid and contorted molecular structure and to their ineffective packaging, they have a large free volume and a high surface area. Besides, thanks to their organic nature, they allow a post- or pre-synthesis modification according to the target application, which is an advantage over the most commonly used non-organic microporous materials [1]. They can also be processed in solution and cast as films, allowing their scalability and application as a bulk material component in different energy systems [2].

This communication deal with the development of new PIMs from low-cost monomers and sustainable synthetic routes [3] for their applicability as advanced polymer microporous membranes to electrochemical energy processes.



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Hydrolytic and enzymatic degradation of polyesters and their block copolymers with PDMAEMA

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Among the various types of biodegradable polymers, the most studied are aliphatic polyesters, including homo- and copolymers of glycolide, D,L-lactide and ε-caprolactone (CL)[1].The biodegradation process of polyesters depends on many factors, such as molecular weight, chemical composition, crystallinity, and hydrophobic/hydrophilic balance[2].The physicochemical properties of polyesters can be modified by combination with another nature of polymers to extend theirapplication directions.In this way copolymers containing both biodegradable polyester blocks and poly(*N*,*N'*-dimethylaminoethyl methacrylate) (PDMAEMA) ones are amphiphilic, as well as they are able to react to changes in pH and temperature.These properties are advantageous to achieve triple-responding drug delivery systems.

Linear aliphatic polyesters, that is poly(ε-caprolactone)(PCL), polylactide (PLA) and poly(lactide-*co*-glycolide-*co*-(ε-caprolactone))(PLGC) were obtained by ring-opening polymerization (ROP), whereas the extra segment of PDMAEMA was introduced by atom transfer radical polymerization (ATRP). These hydrophobic polyesters and amphiphilic polyester-*b*-PDMAEMA copolymers were examined for their susceptibility to undergo hydrolytic and enzymatic degradation at certain pH values [3].

In the case of hydrolytic degradation, SEC analysis for the PCL showed a slight decrease in molecular weight at both pH 5.0 and 7.4, whereas for PCL-*b*-PDMAEMA it was gradually decreased at pH 7.4 and an abrupt decreased at pH 5.0. The results obtained from the ^{1}H NMR spectra, regardless of the pH conditions, for the samples of PCL homopolymer indicatedno weight loss above 10%, while PCL-*b*-PDMAEMA degraded faster in an acidic environment (36% of molecular weight loss determined after 10 weeks) than in a slightly alkaline environment (27% of molecular weight loss after 10 weeks).

In the case of enzymatic degradation,PCL and PLGC were gradually decomposedand after 18 days almost completely disappeared.In addition, there was a sharp decrease in molecular weight forPLA, PLGC and PLGC-*b*-PDMAEMA in the first day.Consistent with the hydrophilic fraction content in the block copolymers, degradation was inhibited with the increase in PDMAEMA block length.This effect can be explained by interactions between hydrophilic PDMAEMA and the immobilized lipase enzyme.PDMAEMA also canblock degradablesites or/and inactivate the protein [4].

The studied semi-degradable polyester/polymethacrylate block copolymers may find application in biomaterials with long or medium term applications, such as nanoscale drug delivery systems with controlled degradation kinetics.

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Investigation of thermal properties of new polythiocarbonates based on dithiol

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Nowadays, polycarbonates (PC) are among the most important class of commercially availablepolymers.Polycarbonates are a group of polymers from the group of polyesters, generally - esters of carbonic acid.Bisphenol A polycarbonates (BPA-PC) areproduced from bisphenol A and phosgene through an interfacial reaction or with diphenyl carbonate [1].BPA-PC is a leading engineering thermoplastic in terms of outstanding transparency and high glass transition temperature.Because of these attributes, it is widely used as a material for electric and electronic, automotive, and optical components [2].Despite its widespread utilization, the exploration of biobased alternatives to BPA-PC is an area of intense scientific interest since BPA is nonrenewable, toxic and is regarded as endocrine disruptor [3.] To overcome these drawbacks, processes using organic carbonates as a carbonyl source have been developed such as condensation of diols and organic carbonates and ring-opening polymerization of cyclic carbonates. Much effort has been devoted to replacing this compound with bio based monomers [4-6].

The aim of our work was to synthesized a new polycarbonate based on dithiol together with diphenyl carbonate.DPC is a necessary precursor for PC production.In the first stage of work the dithiol based on diphenylmethane was synthesized. The structure was confirmed by ^{1}HNMR and ^{13}CNMR (Nuclear Magnetic Resonance) spectroscopy. Next, the transesterification and polycondensation reaction was performed with diphenyl carbonate. Three different catalysts were used. The obtained materials were studied for thermal tests by means of DSC (Differential Scanning Calorimetry) analysis.

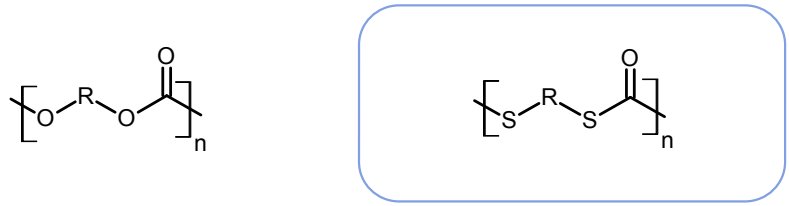

Figure 1: Difference between typical polycarbonates and sulfur polycarbonates [7].

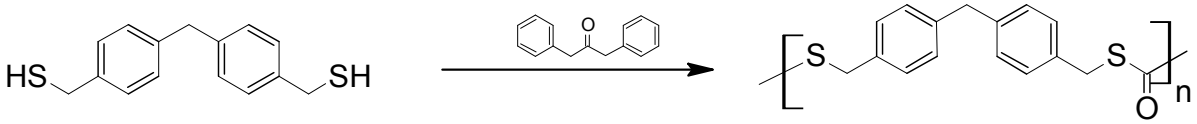

Figure 2: Scheme of polymerization.

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Thermal Stability and Degradation Kinetics of Microcrystalline Cellulose (MCC)/Sol-Gel Silica (SiO_2) Hybrid

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Thermal stability and degradation kinetics of microcrystalline cellulose (MCC)/sol-gel silica (SiO_2) hybrid was investigated using thermogravimetric analysis (TGA). Sol-gel silica was *in-situ*synthesized using tetraethyl orthosilicate (TEOS) as precursor in the presence of MCC. TGA data has shown that thermal stability of MCC/SiO_2 hybrid was enhanced. The iso-conversional kinetic parameters evaluation study of MCC/SiO_2 hybrid was performed under non-isothermal condition using Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) method. The apparent activation energy obtained from FWO method was in good agreement with the value obtained from KAS method. The results shows that an apparent activation energy was increased for the MCC/SiO2 hybrid (171.26 kJ/mol for FWO and 161.67 kJ/mol for KAS) as compared to MCC (151.7 kJ/mol for FWO and 141.04 kJ/mol for KAS).

Synthesis of polymer composites with potential antimicrobial properties

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Zinc oxide is widely used in industry as an additive to paints, a stabilizer for plastics. Thanks to its antimicrobial properties, it is used in cosmetology and medicine. It has a strong antibacterial effect against *Streptococcus mutans* and *Lactobacillus* strains [1]. Zinc oxide has a drying effect, so it is used as an additive to drugs that accelerate wound healing. It absorbs UV radiation very well, therefore it is an ingredient of sunscreen. Due to its low toxicity, ZnOis used in the production of substances appliedto label cellsbiological [2].Zinc oxide has strong antibacterial properties against a wide range of bacteria. The mechanism of its antibacterial action is not fully understood and is the subject of many studies. As one of the mechanisms, photocatalytic production of reactive oxygen species is assumed. Inhibition of bacterial growth may be caused by penetration and disorganisation in the cell membrane, which is due to the interaction of zinc oxide nanoparticles [3].

The aim of this study was the synthesis of polymer composites containing bisphenol A diacrylate(BPA.DA) as amain monomer and 2-ethylhexyl acrylate, (AEH)as an active solvents (Fig. 1.). ZnO was employed as the inorganic, antimicrobialadditive. The synthesis ofcomposites the variable amounts of ZnO(0%, 1%, 2% and 5% by weight,)were applied. The weight ratio of BPA.DA to active diluent was constant 70:30. Polymerization was carried out in special glass forms with dimensions of 10x12 cm.Next, the composite samples were catted(10x15x2 mm) and placed in to glass tubes containing different solvents and water. The aging tests were conducted for 16 weeks. Every week, the samples were weighed wet and then dried for 2 hours in an oven and weighed again. Changes in the chemical structure of composites, under the influence of various factors, were evaluated using ATR/FT-IR spectroscopy.

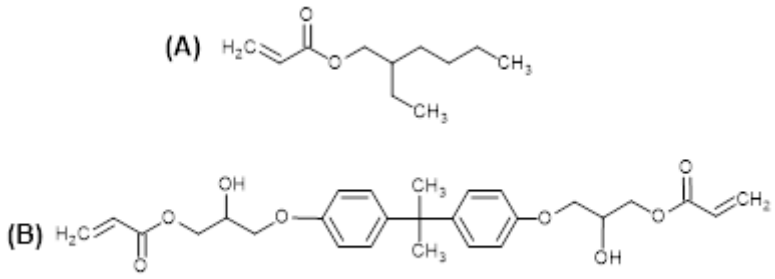

Figure 1. Structural formulas of monomers. A) 2-ethylhexyl acrylate (AEH), B) bisphenol A diacrylate (BPA.DA).

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