



# 1st ECNP Workshop on Progress in Nanostructured Polymers

## PROGRAM AND ABSTRACTS



Lodz University of Technology  
Faculty of Chemistry  
Department of Molecular Physics

*December 14, 2020, Lodz, Poland*

## 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. The 11th International ECNP Conference on Nanostructured Polymers and Nanocomposites and the 7th Conference and Short Course for Young Polymer Scientists, scheduled for September 2020 in Łódź, was postponed to September 26-30, 2021. In order to maintain contacts and exchange knowledge, it was decided to organize on-line the 1st ECNP Workshop on Progress in Nanostructured Polymers.

The ECNP Workshop will start at 8:20 am on 14/12 and will last one day. This event is especially intended for young researchers and students to promote international cooperation. The aim of the Workshop will be to review current research topics carried out by ECNP partners and presented as cooperation proposals and new joint research projects.

We are convinced that thanks to the participation of excellent lecturers from leading European research centers, the set goals will be achieved.

### Local Organizing Committee:

Krzysztof Halagan

Marcin Kozanecki

Beata Luszczynska

Paulina Maczugowska

Lidia Okrasa

Jacek Ulanski

Chairs	<b>Program of 1<sup>st</sup> ECNP Workshop on Progress in Nanostructured Polymers; 14. XII. 2020; Lodz University of Technology, Lodz, Poland</b>		
Jacek Ulanski	8:20 – 8:40	Opening: Prof. Krzysztof Jozwik, Rector of TUL Prof. Malgorzata Szykowska-Jozwik, Dean of Faculty of Chemistry, TUL Prof. Jose Kenny, President of ECNP	
Beata Luszczynska	8:40 – 9:00	M.Sc. Miriam Ferrara	<i>3D printing of high performance polymers for space</i>
	9:00 – 9:20	Dr. Mario Bragaglia	<i>Thermal live monitoring of FFF printing of PA6: the impact of printing conditions on polymer microstructure and properties</i>
	9:20 – 9:40	Prof. Debora Puglia	<i>Lignin basednanocomposites</i>
	9:40 – 10:00	Prof. Jannick Duchet-Rumeau	<i>New Generation of Epoxy Networks</i>
	10:00 – 10:20	Prof. Jean-Charles Majeste	<i>Non-linear Flows of Nano-filled Polymers</i>
	10:20 – 10:40	Dr. Arnaud Favier	<i>Fluorescent Hybrid Polymer Nanoparticles for Bioimaging and Therapeutic Applications</i>
	10:40 – 11:00	<i>Coffee break</i>	
Lidia Okrasa	11:00 – 11:20	Prof. Brigitte Voit	<i>IPF Dresden and its activities in organic and polymeric materials for optoelectronic applications</i>
	11:20 – 11:40	Prof. Andreas Fery	<i>Supra-colloidal structures for photonics and sensing</i>
	11:40 – 12:00	Prof. Markus Stommel	<i>Ultra-Thin Metallic Susceptors for Electromagnetic Induction Heating to induce chemical reactions in high-magnetic fields (&gt;70T)</i>
	12:00 – 13:40	<i>Lunch break</i>	
Marcin Kozanecki	13:40 – 14:00	Dr. Rebeca Hernández	<i>Nanostructured self-assembling polymer materials and gels</i>
	14:00 – 14:20	Dr. Maria Rosa Aguilar	<i>Polymer nanoparticles for biomedical applications</i>
	14:20 – 14:40	Dr. Javier Carretero-Gonzalez	<i>Rechargeable nanostructured polymers activated by CO<sub>2</sub></i>
	14:40 – 15:00	Dr. Maialen Chapartegui	<i>“BUCKYPAPERS” – MWCNT continuous sheets for the manufacture of novel nano-enabled products</i>
	15:00 – 15:20	Dr. Oana David	<i>Polymeric membranes for gas separation</i>
	15:20 – 15:40	<i>Coffee break</i>	
Izabela Bobowska	15:40 – 16:00	Prof. Miroslava Duskova-Smrckova	<i>Macromolecular networks and gels in hydrogels and coatings</i>
	16:00 – 16:20	Dr. Patrycja Bober	<i>Polypyrrole composites- enhancement of electrical conductivity</i>
	16:20 – 16:40	Dr. Hynek Benes	<i>Roles of immobilized ionic liquid on synthesis and properties of biodegradable nanocomposites</i>
	16:40 – 17:00	<i>Coffee break</i>	
Piotr Polanowski	17:00 – 17:20	Prof. Beata Luszczynska	<i>Smart interfaces- role of the interlayers in organic electronic devices</i>
	17:20 – 17:40	Prof. Marcin Kozanecki	<i>Polymer and hybrid (nano)materials for electronic and medical purposes - synthesis, properties and applications</i>
	17:40 – 18:00	Dr. Krzysztof Halagan	<i>Macromolecular simulations of brushes, bottle brushes and polymer networks using cooperative dynamics</i>
	18:00 – 19:00	<i>Discussion and closing remarks (Jacek Ulanski and all partners)</i>	

# LECTURES

## 3D printing of high-performance polymers for space

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Additive Manufacturing (AM) technology has brought about a whole new dimension of manufacturing possibilities in different industries, with aerospace being particularly eager to adopt it. High-performance thermoplastic polymers, such as polyether ether ketone (PEEK) and polyetherimide (PEI), can be used in various space applications due to their high mechanical properties, low density, and low outgassing properties. High-performance polymers could replace conventional metallic counterparts due to their superior strength and stiffness-to-weight ratios. The space industry continues to demand new innovative polymeric materials to reduce weight, increase payload capacity, increase operational range, and enhance the mechanical performance of structures.

Among the high-performance thermoplastic polymers, PEEK and their composites have been proved to be processable via Additive Manufacturing, mainly via Fused Filament Fabrication (FFF), enabling the production of parts both on-ground and out-of-earth [1].

To broaden the application of 3D printed polymeric structure, PEEK has been mixed and blended with different micro and nanofillers (i.e. using carbon nanotubes, magnetite, NdFeB powder, and reduced 5rpheme oxide) to obtain composites and nanocomposites with bespoke functional properties such as electrical conductivity, thermal conductivity, soft and hard magnet properties, absent or entirely different from the one of pure polymer [2-4]. The obtained results are proved to be an interesting alternative to traditional materials for several possible space applications [5-7] (e.g. thermal protection system, electromagnetic devices, magnetic shielding, or and sensors) being lighter, resistant to corrosion [8] and keeping their high mechanical performance.

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## Thermal live monitoring of FFF printing of PA6: the impact of printing conditions on polymer microstructure and properties

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Fused Filament Fabrication (FFF) is one of the most popular additive manufacturing (AM) process that allows to produce polymeric pieces having complex designs and geometries unreachable by traditional subtractive process. A polymeric filament is forced to pass through a heated nozzle and deposited, in the molten state, layer by layer to reach the desired geometry [1]. FFF is very appealing since a low capital investment is needed and the manufactured goods can be quickly and easily produced reducing the material waste. Despite the benefits, up to now FFF technology is still mostly used in rapid prototyping and it does not find an application in mass production preferring the conventional processes [2]. This is due to the fact that there are some limitations in process reliability and product quality [3]. Hence, the mechanical properties of 3D printed products are generally lower than that of the products manufactured through conventional processes. In particular, among the numerous factor affected by processing parameters the cooling rate of the deposited layer is critical since it can vary during the printing. Different cooling kinetics can highly influence the microstructure of the polymer causing different degree of crystallinity and/or crystalline phase transformation [4]. As consequence, the mechanical properties of the 3D printed part will be different layer by layer since the bottom layer may present a higher amount of amorphous material with respect to the top layer showing residual thermal stress and some degree of microstructural anisotropy [5]. The aim of this work is the optimization of 3D printing of a polyamide 6polymer (PA6) by using both optical and infrared cameras as live monitoring sensors during the printing process. The thermal live monitoring has allowed to better understand the cooling kinetics during 3D printing, and to correlate the goodness of 3D printing with microstructure and mechanical properties. A statistical method (Design of Experiment) has been applied to find the most influencing process parameters. The printing parameters have been successively optimized with the aim to maximize the mechanical properties and the geometric tolerances.

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## Lignin based nanocomposites

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Lignin has recently attracted much attention due to its renewable nature, wide variety of source materials available throughout the world, low cost and density, high surface functionality and reactivity. Furthermore, nanocomposite approach has emerged in the last two decades as an efficient strategy to upgrade the structural and functional properties of natural and/or synthetic polymers. The combination of sustainable polymers with bio-based nanostructures opened new perspectives in the self-assembly of nanomaterials for different applications with tuneable mechanical, thermal and degradative properties. The advanced lignin modification chemistry has generated a number of functional lignin-based polymers integrated with both the intrinsic features of lignin and additional properties of polymers, nevertheless limiting the effects to the micro dimension. We started to focus the research on reinforcing polymer composites through nanosized lignins and how they could affect, when dispersed in different biopolymers (gluten, PLA, PVA, chitosan) [1,2], optical, thermal, mechanical, disintegrability, antioxidant activities and antibacterial performance of nanocomposites [3-5]. The potential synergic effect with cellulosic nanostructures [6] has been also investigated, demonstrating how this innovative strategy could enlarge the use of green based nanoparticles to the food packaging sector.

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## New Generation of Epoxy Networks

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Epoxy prepolymers are one of the most important thermosetting polymers due to their excellent properties such as their high electrical insulation, their thermal conductivity, and their excellent thermal and mechanical properties [1]. All these features make them excellent candidates in a wide range of applications such as coating, adhesives and composites [2]. However their low impact resistance due to their high crosslinking density requires the use of different modifiers as the block copolymer, thermoplastic or nanoparticles [3]. Recently, ionic liquids are appeared as new additives to introduce functionalities in epoxy networks by tailoring architectures/morphologies at nanoscale. Their excellent properties such as their low volatility, their non-flammability, their good ionic conductivity, their excellent thermal stability as well as their versatility since it becomes possible to tune the affinity towards the polymer matrix by the control of the chemical nature of the counteranion and/or the cation, bring to the epoxy networks a multifunctional character. In this lecture, different routes to describe the functionalization via the IL will be highlighted: i) the use of ILs as additives of epoxy-amine or epoxy-anhydride systems [4-5], ii) the use of ionic liquids as hardeners of epoxy prepolymer [6] and iii) the synthesis of ionic epoxy monomers based on a bis-imidazolium salt. This last one allows to substitute bisphenol A diglycidyl ether (DGEBA) thus avoiding the use of highly toxic and carcinogenic bisphenol A and epichlorohydrin products and leading to the generation of greener epoxy networks [7, 8]. For each network, the potential of this novel polymer material has been assessed by investigating the effect of the IL on the curing behavior as well as the structure-property relationships of the network including thermal stability, surface properties, mechanical properties, shape memory behavior and electrical conductivity. The innovative design of the ILs monomers offers a wide range of materials able to be processed by 3D and even 4D printing, for processing solid state electrolytes with high performance and new functional and thermostable matrices for composites.

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## Non-Linear Flows of Nano-Filled Polymers

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Among the four core scientific areas of expertise of the IMP laboratory, the team "Structure and Rheology of Polymers: Process and modeling" aims to develop a knowledge base in the field of rheology and polymer processing with the fundamental objective of understanding and controlling the relationships in the triptych structure / rheological properties / processing. The team proposes and structures a set of skills as new experimental methods of characterization, theoretical analyses and development of new forming processes. All of these skills are put into situation in the response to societal challenges in strong interaction with the industrial environment (Recycling of Polymer materials, Natural and Bio-sourced Materials, Lightening of structures...) and enhanced by patents, the creation of startups or the creation of joint laboratories with industrial partners.

One focus in this team is the understanding and the modeling of the behavior of filled polymers in complex flows in relation with process. These systems are of important industrial interest due to applications in many sectors such as automotive, packaging, electrical and electronics and many more sectors. Filler particles are often added to tailor properties such mechanical properties, electrical properties as well as rheological properties for improved processability. It is a well-established fact that addition of filler particles modifies the rheological properties [1], and the composite system behaves different to that of the pure matrix.

In the linear viscoelasticity regime, for micro-composites, the so-called stress amplification in the matrix stems from hydrodynamic interactions which results in enhanced viscoelastic properties. However, when the particles have nanometric sizes, the increase of the specific surface generally leads to gelation of the system related to the attractive interactions between nanoparticles. The particle network is generally out of equilibrium and can form and break up when submitted to non linear shear flow (Payne effect). All these mechanisms have been widely studied in the literature as well as in our laboratory [2-4].

On the other hand, the behavior of these systems under elongational flow remains poorly known although this stronger non-linear flow is present in many processes (thermoforming, blow molding, film blowing, convergent flow in injection process...).

It will be presented a series of experimental and theoretical results performed in our lab on the behaviour of nano-filled thermoplastic polymers under uniaxial elongational flow. Examples will be given to highlight the similarities and differences between micro and nano-filled systems from an experimental point of view. Several model systems have been studied and reveal typical behaviors of filled systems under non-linear flow. Moreover, the modification of the filler/polymer interface is at the origin of additional mechanisms whose microscopic origin will be presented [5-8]. Finally, the understanding of the mechanisms at the scale of a cluster of particles will allow us to propose a modeling in a mean-field fashion which consider the complexity of local flows in the surrounding of the clusters.

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## Fluorescent Hybrid Polymer Nanoparticles for Bioimaging and Therapeutic Applications

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IMP laboratory (Ingénierie des Matériaux Polymères, [imp.cnrs.fr](http://imp.cnrs.fr), Lyon, France) is dedicated to fundamental and applicative research covering the different disciplinary fields of polymer science. In addition, interdisciplinary activities are devoted to polymers for sustainable development and for lifesciences. In the latter case, projects are conducted within three main areas: Polysaccharides and materials for regenerative medicine, Colloids for health and Fluorescent probes for bio-imaging.

Our group is actively involved at the interface between polymer chemistry and biology for many years, with expertise in RAFT controlled radical polymerization [1]. Well-defined polymer probes are synthesized for various bio-imaging and therapeutic applications mainly in infectiology and oncology. These new probes combine biocompatible and multifunctional polymers with organic and inorganic chromophores. They exhibit many advantages such as controlled size and structure, solubility in aqueous media, improved brightness and photostability, tunable photo-physical properties, conjugation with bio-targeting entities (e.g. lipid, peptides, proteins) [2].

Far-red and near-infrared (FR/NIR) bioprobes are particularly attractive since, in this wavelength range, penetration depth of light into biological tissue is improved and auto-fluorescence is limited. However, such molecular or inorganic probes are often poorly soluble and stable in aqueous biological media. An alternative is thus to associate them with water-soluble and multifunctional polymers. Furthermore, it offers the opportunity to concentrate chromophores locally to obtain highly active bio-probes for both imaging and therapeutic applications.

In recent years, we have developed several approaches to combine FR/NIR chromophores with polymers with controlled size and functionality, either as conjugates or nanoparticles [3]. As it will be shown, the resulting polymer and hybrid probes (e.g. polymer/gold hybrids) are soluble and highly biocompatible. The type of chromophore can be varied, for instance fluorophores and photosensitizers that are efficiently excited with a high resolution by two-photon absorption. Applications range from deep imaging in thick tissues or in vivo, super-resolution microscopy, to photodynamic therapy (PDT).

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## IPF Dresden and its activities in organic and polymeric materials for optoelectronic applications

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The Leibniz-Institut für Polymerforschung Dresden e.V. (IPF) is a public polymer research facility which addresses polymer science in an holistic interdisciplinary approach for knowledge based development of structural and functional materials for enabling technologies. The approach covers synthesis and modification of polymer materials, (nano)composites and (bio)hybrids, their characterization and theoretical investigation up to processing and testing for needs in (bio)medicine, energy, mobility, and communication technologies. Accordingly, the IPF is divided in 5 institutes: Macromolecular Chemistry (IMC, Prof. Voit), Physical Chemistry and Physics of Polymers (IPC, Prof. Fery), Polymer Materials (IPW, Prof. Stommel), Biofunctional Polymeric Materials (IBP, Prof. Werner), Theory of Polymers (ITP, Prof. Sommer).

One focus in the IPF Institute of Macromolecular Chemistry, group of Prof. Voit, is the development of functional polymeric materials for printed electronics and various optoelectronic applications. The microelectronics industry and especially the organic/flexible electronics industry continues to demand new innovative polymeric materials. We develop polymeric semiconductor of high charge mobility 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 are fine-tuned in their electronic properties and microstructure by molecular composition design as well as by optimized synthesis methods. In addition, specific dopants for polymeric semiconductor are being developed [2] as well as very flexible polymeric semiconductors and conducting matrices for Maldi-Tof [2].

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. Examples will be given for 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, and for high refractive index materials used as outcoupling layers in high performance state-of-the-art phosphorescent red OLED. Conjugation induced thermally activated delayed fluorescence (TADF) polymers as promising material in OLED could be further prepared [4].

It will be further shown in the group of Petra Pötschkethat conducting polymer nanocomposites, e.g. using carbon nanotubes, carbon nanoplatelets and reduced graphene oxide as filler, are an interesting, cost-efficient and easy to prepare alternative as active materials for sensoric and thermoelectric application [5].

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## Supra-colloidal structures for photonics and sensing

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Metallic nanoparticles offer a range of interesting optical and electronic effects. A prominent example is the localized surface plasmon resonance (LSPR) due to resonant excitations of vibrations of the particles free-electron cloud by light. Due to the LSPR, plasmonic nanoparticles provide excellent means for controlling electromagnetic near-fields at optical frequencies, which has led to a broad range of applications in various field such as surface enhanced spectroscopy, light harvesting or photonics.

While much research is dedicated to understanding nanoparticle synthesis and tailor their LSPR on the single particle level [1], ordering particles on different length scales opens another powerful avenue towards optical and electronic functionality. Plasmonic particles can couple locally, altering their LSPR, but as well collective long range phenomena can give rise to novel effects. In this context, integrating plasmonic nanoparticles into polymeric shells and / or scaffolds opens novel perspectives for solving this technological challenge. In particular we focus on scalable approaches for template assisted colloidal self assembly [2]. We discuss the underlying physico-chemical principles of assembly and plasmonic coupling effects arising in the assemblies [3]. Finally we discuss perspectives for applications in Surface Enhanced Raman Spectroscopy and Photonics, as well as approaches towards tuning of plasmonic coupling effects by mechanical strains [4].

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## **Ultra-Thin Metallic Susceptors for Electromagnetic Induction Heating to induce chemical reactions in high-magnetic fields (>70T)**

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Induction heating is widely employed for the heating and bonding of metals. In principle, an alternating electromagnetic field induces Eddy current in susceptors, often composed from a metal, which delivers energy in form of heat to the surrounding medium. To transfer the macroscopic principle to nanoscopic processing technology and interfacial bonding of polymer materials are a challenge.

Using metal susceptors of a few nanometers in thickness for targeted heating the interface of reactive polymer materials is an auspicious strategy. Ultra-thin metallic structures are applied to reduce heating of bulk material, thus an increase in bonding process efficiency and protection of heat-sensitive materials. Characterization and optimization of susceptor structures regarding their heating efficiency are a major objective.

A permanent adhesion requires the formation of covalent bonds between polymer materials and inert susceptor materials, e.g. silver or gold. Bisphenol-A-based Polycarbonate is an precise engineering material with excellent mechanical and optical properties and can be bonded to amines. This reactive system serves as model to develop a nondestructive, structure-sensitive analytical method to evidence formation of new covalent bonds. FTIR spectroscopic Imaging and multivariate data-analysis seem to be suitable to proof localized heating effect.

## Nanostructured self-assembling polymer materials and gels

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The **Institute of Polymer Science and Technology (ICTP-CSIC)** is a public polymer research facility aimed to the scientific and technological advancement of polymeric materials through research and development. Currently, the ICTP-CSIC is divided in 5 departments: Polymer Physics, Elastomers and Applications Energy, Polymeric Nanomaterials and Biomaterials, Polymeric Physical Chemistry and Applied Macromolecular Chemistry.

Investigation about gels and nanostructured self-assembling polymer materials is a well-established research line in the group of Nanostructured Polymers and Gels group (led by Prof. Carmen Mijangos) within the Department of polymer nanomaterials and biomaterials. In this talk, we will show results from this research line including 1) different methods for polymer gelation (through chemical and physical interactions or formation of interpenetrating polymer networks among others) [1-3], 2) functionalization through reactions of modification or incorporation of nanoparticles for the preparation of nanocomposite polymer hydrogels [4-6], 3) Structure-properties relationship in polymer gels at different scales (nano, micro and macro) with emphasis in the determination of the rheological properties [7-9], 4) development of advanced applications, mainly in the biomedical field (controlled drug delivery and 3D printing) [10–12] and 5) Layer-by-layer assembly as an experimental methodology to obtain gel coatings and nanostructured polymer films for biomedical applications [13, 14].

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## Polymer Nanoparticles for Biomedical Applications

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The Biomaterials Group (ICTP-CSIC, [www.biomateriales.ictp.csic.es](http://www.biomateriales.ictp.csic.es)) is a multidisciplinary group with two main research lines: the development of new systems for the encapsulation and controlled release of bioactive and therapeutic molecules and the development of new scaffolds for tissue engineering. Both lines converge continually, giving rise to high-performance biomaterials and medical devices.

Chronic inflammation diseases are ranked as the first cause of morbidity and mortality worldwide. They also cause long-term suffering, disability reduction on the quality of life and high cost to the society. Actual anti-inflammatory drugs present a limited effectiveness due to their hydrophobicity, low bioavailability, and lack of specific targeting. Moreover, anti-inflammatory treatments have associated several side effects limiting their safe use in the clinic. Our group has dedicated great efforts to the preparation of more efficient derivatives of these drugs: drug conjugates [1], drug combinations showing synergistic effects [2] and nanometric drug delivery systems (NDDS) [3,4].

In this presentation the application of polymer nanoparticles as drug delivery systems for the treatment of inflammatory diseases will be presented. In particular, non-steroidal anti-inflammatory drugs, NSAID (*i.e.* naproxen or ketoprofen) were chemically modified and the methacrylic derivative of the correspondent NSAID was prepared (*i.e.* HNAP or HKT, respectively). These synthetic monomers were used for the synthesis of polymer drugs with a pseudo-gradient microstructure by free radical copolymerization with 1-vinylimidazole (VI). These amphiphilic pseudo-block copolymers self-assembled in aqueous media by nanoprecipitation forming nanoparticles with spherical shape, nanometric size (between 100 and 200 nm) and positive surface charge. These physico-chemical properties demonstrated non-toxicity and a fast sequestration by macrophages which favors accumulation and retention at inflamed areas. Other hydrophobic drugs were loaded in the hydrophobic core of the nanoparticles (*e.g.* dexamethasone) and the synergistic pharmacological properties were studied *in vitro*. The combination of naproxen and dexamethasone showed a synergistic reduction of *Il12b* transcript levels which makes this combination highly interesting for the treatment of autoimmune/inflammatory diseases, being a cost effective alternative to commercial biological treatments as ustekinumab [2].

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## Rechargeable nanostructured polymers activated by CO<sub>2</sub>

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Herein I will describe a series of innovative nanostructured polymers exhibiting high redox activity and water stability so then being potential low-cost, rechargeable electrolyte materials for aqueous electrochemical devices. One of the novel systems consists of nanoparticles comprising innocuous and functional (including redox) interpenetrated macromolecular networks. Remarkably, the addition of carbon dioxide further boosted the electroactive processes. A complete study of the physical, chemical and electrochemical properties of these advanced nanostructured functional polymeric materials will be presented and the results derived are discussed in the scope of their potential application as rechargeable electrolyte materials for polymer batteries.

### *Acknowledgment:*

J.C.G. acknowledges support from the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) through a Ramon y Cajal Fellowship (RYC-2015-17722) and the Retos Project (MAT2017-86796-R, AEI/FEDER/UE).

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## **“BUCKYPAPERS” – MWCNT continuous sheets for the manufacture of novel nano-enabled products**

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Recent activities at Tecnalia have focused on the creation of nano-enabled products based on carbon nanotubes (CNTs) with applications aimed primarily at composite structures for the transport sector [1]. There is now an increasing demand for these products in other sectors such as energy, construction, water treatment and health.

Previous methods to introduce CNTs into composite structures have identified considerable drawbacks. Early research involved direct mixing of the nanotubes with polymer matrices to create the nanocomposites. However, high van der Waals forces led to agglomeration of the nanotubes, leading to poor CNT dispersion which resulted in a huge increase in the viscosity of the resin system. Manufacturing fibre reinforced composites with liquid technologies (infusion, RTM, etc.) also led to CNTs being trapped by the fibre reinforcement during the resin flow, causing a “filtering effect” [2].

To avoid these issues Tecnalia has developed a CNT sheet, or “buckypaper”, manufacturing technology that enables the introduction of high localised loadings of CNTs into a structure whilst avoiding all the previous drawbacks. The CNT “buckypaper” (BP) interlayer is a low weight sheet consisting of entangled carbon nanotubes that has been manufactured in a continuous filtering mode on a pilot plant designed and developed by Tecnalia. This pilot plant offers the production of continuous filtered films at scales suitable for industrial uptake and enables the manufacturing of buckypapers with widths up to 300 mm and lengths up to 100m. The process enables the control of the BP thickness in the range of 30-200 microns and areal weights in the range of 30-200 g/m<sup>2</sup>. The material has a typical porosity of 45 – 75 %, and average pore size of 40-60 nm. Through the control of the thickness, porosity, pore size and areal weight it is possible to manufacture material with a range of properties that can be tailored to a wide range of applications.

This presentation summarizes Tecnalia’s activities related to the development of a wide range of industrial solutions based on the CNT buckypaper material for applications such as:

- Enhanced electrical properties for composite structures (e.g. lightning strike protection).
- Integrated composite heater element (aircraft, passenger vehicles, ...).
- Flexible SHM sensors (crack development, structural cyclic loading, ...).
- Fire resistant barrier layer.
- Interlayers and electrodes for more efficient batteries and supercapacitors.
- Nanofiltration layer for water purification.

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## Polymeric membranes for gas separation

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Membrane based gas separation processes have gained much attention in the past few decades. Compared to conventional gas separation technologies like cryogenic distillation, condensation and amine absorption, membrane separation processes have lower energy consumption, relatively small footprint, low mechanical complexity and the main advantage of operating under continuous, steady state conditions [1].

In order to assess gas separation at large scale, membrane products need to be highly productive. For this reason, there are two features that commercial membranes generally meet. First, the membranes are asymmetric with a dense and thin (100–200 nm) top layer supported by a thicker porous sublayer. The actual membrane is the top layer whose thickness controls the productivity of the membrane. Second, most commercial membranes are processed in the form of a fiber (<500 µm) with a hollow interior, because hollow fibers can be densely packed at over 10,000 m<sup>2</sup> membrane active area in 1 m<sup>3</sup> module volumen [2-4] ten times more than for flat sheet membranes in plate and frame packaging. Therefore, the fabrication of hollow fibers with an ultrathin and defect-free dense selective layer is essential, since permeance and selectivity of the membrane will be determined by the quality of the selective layer. However, the thinner the selective layer is, the greater the probability for the creation of defects [5-7].

Membranes are used in several gas separation applications, being the more stablish processes the hydrogen recovery (H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/CO separation), nitrogen production (O<sub>2</sub>/N<sub>2</sub> separation), natural gas treatment (CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>S/CH<sub>4</sub> and He/CH<sub>4</sub> separation) and vapor recovery. However, membranes used in these applications are based on a small number of polymers, such as polysulfone, polyimides, cellulose acetate polyphenylene oxide and silicone rubber [8].

Polyimides are among the most interesting polymeric materials for gas separation applications due to their good trade-off between perm-selectivity and permeability, high thermal and chemical stability, combined with high mechanical strength, long durability and their suitability to prepare asymmetric structures [9].

There are several potential new applications, such as olefin/paraffin separation, CO<sub>2</sub> capture (CO<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CO<sub>2</sub> separation) and vapor/vapor separation, were new membrane materials with improved separation properties are required.

In this work we will show experimental results for the preparation of selective and asymmetric hollow fiber membranes based on different polyimides (PBI and P84) with and without inorganic fillers for CO<sub>2</sub> separation in pre- and post-combustion CO<sub>2</sub> capture applications.

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## Macromolecular networks and gels in hydrogels and coatings

### Karel's Invitation to a Journey

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On **October 30, 2020 at 10:32** in the morning the grand heart of professor **Karel Dušek** peacefully stroke for the last time. While this sad news still gradually penetrates through the macromolecular community, our grieving hearts turn to memories of Karel's continually inspiratory mind. Our thoughts dialogue with challenges, ideas, and physical models that he would propose with a zeal and great interest to know the result.

Thus today, Karel's departure has become an impetus for this lecture to be given. The goal of the lecture is to introduce a fraction of the latest scientific contributions of KD in the field of macromolecular networks and gels. Last and not least, the lecture is a tribute to one of the founders of the ECNP project.



Karel Dušek  
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\*May 6, 1930 – † October 30, 2020 Prague

In the area of *swelling* of gels [1], recently, KD and MD have revisited the intriguing topic of volume phase transition in swollen macromolecular gels – so far theoretically. Although already fifty years have elapsed from the prediction of existence of volume phase transition (VPT) in swollen polymer gels by Dušek and Patterson [2] and forty years from its experimental discovery by Tanaka [3], the number of papers dealing with this phenomenon reached the order of  $10^4$  since then and keeps increasing. Here, we will show that some swollen gels characterized by continuous change of the degree of swelling transform into ones where the degree of swelling changes abruptly – gels reveal VPT under acting strain [4]. The external force can make the transition wider and more robust in gels where transition is already observed under free swelling condition. The possibility to induce the volume phase transition by external stresses can be utilized for finding new stimuli sensitive gels, strengthening of gel response, and in modelling of properties of gel constructs by Finite Element Method.

In the area of *functional precursors for coating systems*, the investigations are inspired by certain obstacles during the application process. The conditions required for chemical drying (= covalent cross-linking) and protective ability of thermosetting coatings are quite demanding, especially if drying is to proceed at room or mildly elevated temperatures and the coating film is to be tough and hard, like in the case of vehicles repair. Rather than searching for new chemistries, the research efforts concentrate on multistep processes in which oligomeric precursors are synthesized from small molecules which are then cured with a cross-linker, possibly also oligomerized [5]. The main advantages of proceeding via precursors are adjustment of functional group reactivity and speed of cure, optimization of the viscosity build-up and pot life related to the gel point, reduction of health hazards by lowering the volatility and penetration ability of toxic groups and reducing VOC [6]. Optimization of properties means adjustment of  $T_g$  build-up and hardness development relative to the reaction speed; these effects are mutually counteractive since reduction of segmental mobility reduces considerably reaction rates: indeed, undercured films do not perform well. One of the important goals of properties optimization is securing good toughness, because increase of hardness does not mean maintaining or increasing toughness. The emerging trend is combination of chemical, covalent cross-linking with formation of network of labile, physical bonds. The physical bonds may range from strong dipolar interactions,

via hydrogen bonds, to labile chemical bonds studied in connection with self-healing. It is important that not only increased thermal fluctuation can lead the rearrangement of thermoreversible, physical network, but also the stress fields imposed from outside impact may bring the necessary energy albeit in different frequency range. What theoretical methods are available for reaching these goals? A characteristic feature of oligomeric precursors are their distributions of molecular weights and composition, and numbers of functional groups of several types. In oligomer synthesis, model kinetic experiments characterizing relative rates of individual steps, aided by estimation of group reactivities by quantum chemical methods, give input for calculation of the distributions by numerical solution of systems of kinetic differential equation. Verification of modelling results by molecular ion mass spectrometry (e.g., MALDI-TOF-FT-MS) may also discover side reactions not expected or underestimated by the chemist; the reaction scheme is then corrected. Important is that these distributions, preferably in the form of generating functions, can be used in the next step – cross-linking of the oligomer. For this stage, we have branching theories available which describe evolution of the system in terms of change of molecular weight distribution, the gel, point, sol and gel fractions, composition, and concentration of elastically active chains determining the modulus of elasticity in the rubbery state. For estimation of hardness and toughness development, thermomechanical and spectroscopic methods should be combined, aided by quantum chemical estimation of H-bond strength, dynamic-mechanical and dielectric relaxations, and segmental mobility characterization based on modern T<sub>g</sub>-transition theories.

In this contribution, we will show results along these lines on hydroxy-functional star shaped binders and their cross-linking with a tri-isocyanate, as well as a fast curing binder based on oligomers of aspartate type. Already in the oligomeric stage, small changes in the initial composition may cause development of side reactions based on transesterification or amine ester transformation to amide and alcohol functions. These changes are then transposed to the curing stage and may affect properties especially moisture absorption.

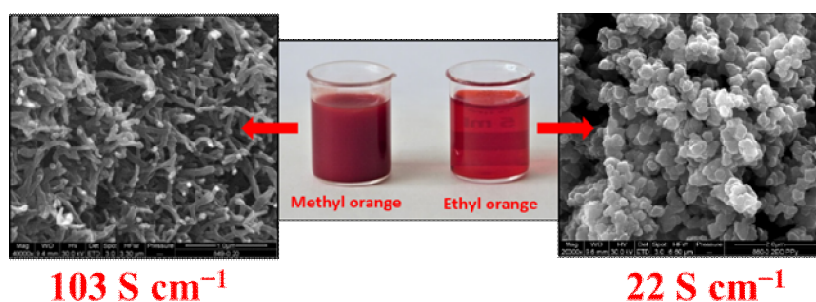
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## Polypyrrole composites- enhancement of electrical conductivity

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Polypyrrole (PPy) is one of the most known conducting polymers due to its high electrical conductivity, easy preparation, biocompatibility and excellent environmental stability [1]. The properties of PPy, important for various practical applications, e.g. supercapacitors, like conductivity, specific surface area, electroactivity, etc., can be easily modified and improved during the synthesis. The addition of organic dyes into pyrrole polymerization has been found to significantly improve its conductivity and modify the morphology. Methyl orange leads to PPy nanotubes with conductivity reaching  $103 \text{ S cm}^{-1}$  [2], Acid blue 25 added to the polymerization medium guides the formation of nanofibers with conductivity of  $60 \text{ S cm}^{-1}$  [3] and safranin to obtain PPy nanorods with conductivity of  $35 \text{ S cm}^{-1}$  [4]. The polymerization temperature was found to have also powerful effect on the conductivity [5]. When the polymerization of pyrrole was performed in frozen state ( $-24 \text{ }^\circ\text{C}$ ), the highest conductivity of  $175 \text{ S cm}^{-1}$  was achieved for PPy nanorods prepared in the presence of safranin [6]. This principle has also been applied to the preparation of stable colloids of PPy nanotubes/nanorods, which due to the extended morphology allows for casting the films with conductivity nearly two orders of magnitude higher than those obtained from colloids of ordinary PPy nanoglobules [7].



**Fig. 1.** Morphology and conductivity of polypyrrole prepared in the presence of methyl orange (left) and ethyl orange (right).

Conductivity can be also improved when preparing composite materials. The conductivity of the PPy/molybdenum disulfide composite with a moderate content of PPy (15–30 wt.%) reached  $13 \text{ S cm}^{-1}$ , which is markedly higher than the conductivity of both the pristine PPy and  $\text{MoS}_2$ ,  $1$  and  $10^{-6} \text{ S cm}^{-1}$ , respectively [1]. Additionally, the preparation of composite PPy cryogel supported by gelatin results in macroporous materials with enhanced conductivity,  $18 \text{ S cm}^{-1}$ , preserved even upon deprotonation in water under physiological conditions [8]. Such PPy composites with increased conductivity can be used in different applications such as electrodes materials, supercapacitors, conductive fillers, etc.

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## Roles of immobilized ionic liquid on synthesis and properties of biodegradable nanocomposites

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Layered double hydroxides (LDH) functionalized with phosphonium-based ionic liquid (IL) as novel catalytic/initiating system for ring opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ CL) has been investigated. The progress of microwave-assisted polymerization in the presence of the modified LDH was studied showing the anionic mechanism of ROP initiated by the water molecules, which were adsorbed on the LDH surface and intercalated in the LDH galleries. The whole polymerization was significantly accelerated by microwave energy, which induced molecular rotations of the intercalated IL-anions leading to LDH delamination and exfoliation into individual nanosheets, which made the catalytic sites (IL-anions) easily accessible for the  $\epsilon$ CL molecules. The kinetics of microwave-assisted ROP thus showed a 4.6-fold increase of the reaction rate compared to the polymerization performed under conventional heating. Activation enthalpy and entropy were calculated for the microwave-assisted polymerizations initiated by the modified LDH. The use of microwave-active catalytic-initiating LDH nanoparticles enables to synthesize the organometallic catalyst-free polycaprolactone (PCL) or, at higher LDH loadings, the highly-exfoliated PCL/LDH nanocomposites, which are highly desirable for e.g. packaging materials [1].

Moreover, the high capacity of calcinated LDH to immobilize various active molecules together with their inherent gas/vapor impermeability make these nanoparticles highly promising to be applied as nanofillers for biodegradable polyester packaging. Therefore, we have investigated trihexyl(tetradecyl)phosphonium decanoate IL for immobilization on the surface of calcinated LDH. The synthesized nanoparticles were used for the preparation of PCL/LDH nanocomposites. Two different methods of nanocomposite preparation were used and compared: microwave-assisted *in-situ* ROP of  $\epsilon$ CL and melt-blending. The *in-situ* ROP of  $\epsilon$ CL in the presence of LDH nanoparticles with the immobilized IL led to homogenous nanofiller dispersion in the PCL matrix promoting formation of large PCL crystallites, which resulted in the improved mechanical, thermal and gas/water vapor barrier properties of the final nanocomposite. The surface-bonded IL thus acted as nanofiller surfactant, compatibilizer, as well as thermal stabilizer of the PCL/LDH nanocomposites. Contrary to that, the melt-blending caused a partial degradation of the immobilized IL and led to the production of PCL nanocomposites with a heterogenous nanofiller dispersion having inferior mechanical and gas/water vapor barrier properties [2].

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## Smart interfaces- role of the interlayers in organic electronic devices

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Since years, we are trying to extend our understanding of the nature of physical phenomena occurring in the organic semiconductors and the devices with organic active layers, such as: organic light emitting diodes (OLEDs) [1, 2], photovoltaics (OPV) [3, 4], photodiodes (OPD) [5] and field effect transistors (OFETs) [6].

Organic electronics based on soluble materials create prospects for mass and cheap production of new devices, such as large-area and lightweight OPVs, OLEDs or OPDs. However, the development of printed organic electronics has faced a barrier that results from a lack of full control and understanding of physical and physicochemical phenomena at the interfaces [5, 7, 8]. In particular, the performance and lifetime of practically all organic electronic devices is affected by the metal-organic interface of the cathode. There is an urgent need to develop solution-processable and stable cathodes which could replace unstable, vacuum deposited calcium and magnesium cathodes. It requires fundamental progress in the understanding of the electrode interface both during the deposition and the operation of the device. The most promising way to achieve this goal is an introduction of electrode modifying interlayer between the metal, such as silver, and the organic semiconductor of the active layer of the device.

Herein we will present two examples of successful application of the interlayers significantly improving the performance of OPD and OLEDs. In both cases we have used the solution processable compounds. In the case of OPD, the introduced interlayer has modified the work function of ITO electrode, what allowed to construct photodetector with inverted structure, which characterised with low level of dark current [5].

In OLEDs the printing of caesium carbonate interlayers improved the effectiveness of the injection of electrons into the active, emissive. Moreover we used the ink-jet printing technique as the method of patterning of the emission area of OLEDs [9].

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## Polymer and hybrid (nano)materials for electronic and medical purposes - synthesis, properties and applications

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Modern methods of material synthesis allow for designing products with well controlled architecture and desired properties. The most effective in this field are syntheses based on bottom-up strategy. This approach can be applied to produce both organic [1] and inorganic compounds [2]. In this lecture two issues will be discussed: (i) well-defined hybrid nanomaterials synthesized with use of Atom-Transfer Radical Polymerization (ATRP) for electrical devices and Surface Enhanced Raman Spectroscopy, (ii) poly(oligo(ethylene glycol) methyl ether methacrylate)-based (POEGMA) hydrogels for biomedical and engineering purposes.

The controlled synthesis of hybrid nanoparticles with use of ATRP methods will be shown. Two strategies of nanostructure preparation will be presented. The first one based on the copolymer templates with tailored architecture and molecular mass loaded by the suitable precursors allowed to obtain nanomaterials useful for flexible organic electronic devices (for gate dielectric layers), or for surface enhanced Raman spectroscopy [3]. An alternative approach based on surface-modification of metals or metal oxides by polymer chains will be discussed in relation to control preparation of hybrid core-shells nanostructures [4].

Currently, POEGMA-based networks are regarded as promising biomedical materials, because of their biocompatibility, non-toxicity and possibility to easy control of physical properties. They are also able to form thermo-responsive hydrogels with the volume phase transition (VPT) temperature dependent on the length of oligo(ethylene glycol) (OEG) segments [7]. Within the lecture we will show how the architecture (network regularity, density and additional “decoration”) impact on the physical properties of POEGMA-based networks and hydrogels [6]. The water structure inside the gels, and the mechanism of network hydration will be discussed in detail [7]. Influence of some selected non-steroidal anti-inflammatory drugs on the VPT will be shown [8]. The tendency for crystallization found for POEGMA networks with suitable long OEG segments will be also discussed [9].

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## Macromolecular simulations of brushes, bottle brushes and polymer networks using cooperative dynamics

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The importance of simulation of complex polymeric systems (like multiarm stars, hyperbranched polymers, dendrimers, comb-like or dendronized polymers, grafted brushes, polymer gels and networks) is evident. Moreover, due to the fact that simulations of polymer blends, melts, solutions and composites (and soft matter in general) are pretty challenging – their properties usually involve a variety of time scales and broad range of sizes – there is still a large need of dynamic methods that can give some insight into polymer systems properties. This involves diffusive behavior, morphology, solvent dynamics, static properties and properties of controlled synthesis process of polymer macromolecules. In our department we successfully use Dynamic Lattice Liquid (DLL) model, originally proposed by T. Pakula [1]. This is lattice Monte Carlo method treating matter as a coarse-grained system with realistic time scale. Algorithm based on DLL model is much faster than molecular dynamics simulation and makes possible simulation of large number of grains (no atomistic details) and for low polymerization rates in a reasonable time. The unique dynamic properties and parallel nature of DLL gave basis for the idea of massively-parallel simulator – ARUZ (Analyzer of Real Complex Systems) [2].

In this presentation we show simulation studies with DLL and ARUZ, performed in frame of three project founded by Nation Science Centre Poland. In first project (NCN 2014/14/A/ST5/00204), devoted to polymer templates used as nanoreactors for metal nanoparticles synthesis, simulations covered: influence of crosslinking on network gelation [3], static and dynamic properties of short bottle-brushes [4], polymer stars with highly compact multi-functional cores [5], polymer brushes on flat surfaces [6,7] and polymer brushes in pores [8]. In the second one (NCN 2017/25/B/ST5/01970) ARUZ machine is used to simulate: polymer double-brush structures and dynamics [9], precisely defined bottle-brushes in good solvent conditions and in low solutions which are directly compared with experimental studies [10], and diffusion of oligomers inside well-defined polymer matrixes. The last project (NCN 2017/25/B/ST4/01110) covers simulation of polymer networks synthesis using kinetically controlled radical polymerization [11].

*Acknowledgment:* The studies were supported by Polish National Science Centre grants 2014/14/A/ST5/00204, 2017/25/B/ST4/01110 and 2017/25/B/ST5/01970.

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