WORKSHOP

CAREER IN POLYMERS XI

PRAGUE, 28-29 JUNE 2019
INSTITUTE OF MACROMOLECULAR CHEMISTRY CAS

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HEYROVSKÉHO NÁM. 2, 162 06 PRAGUE 6, CZECH REPUBLIC

BOOK OF ABSTRACTS

WORKSHOP CHAIRMAN
LIBOR KOBERA
Photo on the Cover: A. Libánská, Biodistribution of HPMA linear copolymer with Cy 5.5 in the mice with acute arthritis in right ankle, time 24 hours (from lecture L9).

EDITORIAL INFORMATION

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WORKSHOP CAREER IN POLYMERS - NEW DIMENSION OF PRAGUE POLYMER MEETINGS

The Institute of Macromolecular Chemistry, Czech Academy of Sciences has become an important center of European polymer research since its foundation in 1959. Currently, it encompasses virtually all branches, directions and trends in contemporary polymer science. Besides, the Institute became famous as an organizer and venue of many congresses, conferences, world symposia, microsymposia, discussion conferences and summer schools devoted to polymer science in general and various special aspects of polymer chemistry, physical chemistry, physics and technology, in particular. The specialized symposia became known as Prague Meeting on Macromolecules (PMM).

In 2009, a new dimension of these Prague polymer meetings emerged. Immediately after the 73rd PMM Conference, a special workshop named “Career in Polymers” was organized under the auspices of the Central and East European Polymer Network, CEEPN. It was aimed predominantly, but not exclusively, at young polymer scientists from Central and East European countries. The aim was to provide a forum for mutual contacts between young scientists just starting their career in polymers, to initiate their discussions with renowned scientists within the Institute, to promote polymer science and to show its charm and beauty. “Career in Polymers” covers all aspects of polymer science – polymer physics, polymer chemistry and applications of polymers especially in medicine, electronics, and as hybrid and composite materials. The recently established tradition of the Prague meetings for young scientists continues also in the year 2019. The workshop “Career in Polymers XI” will include the closing seminar of the UNESCO/IUPAC Postgraduate Course in Polymer Science – the 23rd run of the Course organized in the academic year 2018–2019. Furthermore, a part of this workshop is a meeting between young scientists and representatives from industry supported by Strategy AV21 “Top research in the public interest”.

![Image of the Institute of Macromolecular Chemistry, Czech Academy of Sciences](image-url)
The Postgraduate Course in Polymer Science has been organised by the Institute of Macromolecular Chemistry AS CR since the academic year 1996–1997 under the auspices of international organisations UNESCO and IUPAC and with financial assistance of the Academy of Sciences of the Czech Republic. Cumulative results of the 22 runs of the Course by the end of the year 2018 are 188 graduates from the following 24 countries: Algeria, Bangladesh, Brazil, Bulgaria, Cameroon, China, Croatia, Egypt, Hungary, India, Iran, Kazakhstan, Macedonia, Mexico, Nepal, Poland, Romania, Russia, Serbia, South Africa, Ukraine, Uruguay, Uzbekistan and Vietnam. The Course lasts 10 months and is comprised of about 50 hours of lectures in modern polymer science and of participation in all educational activities within the Institute. Most of the time, however, is devoted to experimental work on research projects under the supervision of senior scientists of the Institute. Active research is the keystone of the Course. Regularly, the participants report on progress of their research at working meetings of their teams and participate at seminars and technical meetings within the Institute. At the end of each run, a seminar in the form of an international workshop is organised, at which all the participants present their results. Subsequent development of career of the Course participants shows, that completion of the Course has been very helpful to professional promotion of the graduates in their home countries. Co-operation with a number of them continues through joint projects with their home laboratories. More than 30 graduates have commenced a Ph.D. degree programme at Czech universities in cooperation with the academic laboratories; several others work as postdoctoral researchers at the Academy of Sciences of the Czech Republic. The graduates of the Course have published the results of their research in more than 500 papers in international scientific journals cited more than 10000 times and many communications at international meetings. Detailed information on the Course can be found at http://www.imc.cas.cz/cz/umch/kursy_unesco_iupac.htm.

At the General Assembly of the International Union of Pure and Applied Chemistry, held in Beijing, China in August 2005, the organisers of the Course were awarded the 2005 IUPAC-Samsung Education Prize by the President of the Union, the Prize was sponsored by the Samsung Company.
**PROGRAMME**

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SCAVENGING OF REACTIVE OXYGEN SPECIES BY PHENOLIC COMPOUND-MODIFIED IRON OXIDE NANOPARTICLES
Conducting polymers are prepared by the oxidation of monomer with oxidant in acidic aqueous medium at room temperature and collected as a precipitate. When the polymerization of monomers is carried out in the presence of a water soluble-polymer in frozen reaction mixture, soft conducting hydrogels are obtained after thawing. They can be freeze-dried to obtain aerogels which in turn can be converted by carbonization in inert atmosphere to nitrogen-containing carbogels. Such materials, three-dimensional conducting polymeric networks, can be potentially used in medicine, biology, water-treatment or in energy storage devices.

Fig. 1. Composite polypyrrole/gelatin cryogel prepared with 5 wt% of gelatin (left) and illustration of macroporous morphology of corresponding aerogel (right).

Keywords: polyaniline, polypyrrole, cryogels, aerogels, carbogels, composites.

Acknowledgement: The authors wish to thank the Czech Science Foundation (18-04669S) for the financial support.

References:
The renewability of lactide and inexpensive raw material (e.g. starch, glucose…) for its production makes it an interesting monomer for producing biodegradable polymer; polylactide (PLA) suitable for many applications, e.g. in medicine, health care and cosmetics, agriculture, etc., in which waste recovery and recycling is not possible or practical.

Ring opening polymerization (ROP) of lactide (typically racemic mixture of D- and L-lactide produces amorphous PLA (PDLLA) with beneficially high rate of biodegradation. However, the challenging part is that PDLLA has limited oxygen and water vapor barrier properties, poor crystallization behavior, high brittleness and low thermal resistance. To enhance these properties, the in-situ synthesis of PLA nanocomposites is described in this contribution.

First, organically modified layered double hydroxides (LDH) were prepared and characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). Bulk ROP of the (d,l-) lactide has been performed in the monomode microwave reactor in the presence of a conventional catalyst (stannous catalyst) and/or modified LDH. Kinetics of the polymerization (at temperature range between 120°C and 180°C) was followed using the gas permeation chromatography (GPC) by measuring monomer conversion and molecular weight. Influence of the filler on the morphology, thermos-mechanical, gas and water vapor barrier properties of the PLA nanocomposites were determined.

Keywords: (d,l-)lactide, bulk ring opening polymerization, microwave synthesis, polylactide, layered double hydroxides.

Acknowledgement: The authors thank the UNESCO/IUPAC Postgraduate Course in Polymer Science 2018/2019, for financial support of this work.
Electrically conductive polymer composites (CPCs) are materials that are attracting certain attention nowadays due to applications in various areas, like packaging, electronics or sensor technology. These composites consist of an insulating polymer matrix and a conductive filler. In the frame of this project, special attention is paid to immiscible polymer blends with selectively localized carbon black. Carbon black particles easily form chain-like aggregates and consequently a conductive network, resulting in percolation threshold at relatively low filler concentration.

In this study, carbon black is added at various volume concentrations to different thermoplastic polymers and their blends. The aim is to determine the influence of carbon black particles and their localization on viscoelastic properties. Furthermore, the effect of carbon black on structural changes in the blends is investigated by means of electron microscopy. Thus, controlling the blends morphology and filler localization it is possible to tailor the electrical conductivity.

**Keywords:** polymer composites, rheology, electrical conductivity.

**Acknowledgement:** Financial support of the Czech Science Foundation (grant 17-05654S) is highly acknowledged.
INVESTIGATION OF HYBRID PEROVSKITE AND POLYMER THIN FILMS FOR PHOTONICS AND ELECTRONICS

M. Guesmi, D. Výprachtický, V. Cimrová

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Organic-inorganic perovskites are an interesting class of semiconductor materials due to the characteristics of both inorganic and organic materials such as low cost, long carrier diffusion lengths, high carrier mobility, high absorption coefficient in the visible region, easy production and large area of optoelectronics devices such as light emitting diode (LED) and photovoltaic cells (PVs).\(^1\) However, these materials are very sensitive to moisture and oxygen, which could cause severe property degradation and thus affect the quality of the resulting film and finally the device performance. Therefore, the investigation of the thin films, their properties and stability are of interest.

In this contribution, we report on preparation, characterization and photophysical properties of thin films made of organic-inorganic perovskites (methylammonium lead iodide (CH\(_3\)NH\(_3\)PbI\(_3\)) and formamidinium lead iodide ([NH\(_2\)=HCNH\(_2\)]PbI\(_3\)) and their hybrid systems with selected conjugated polymers to try to improve their stability and properties. One and two step spin-coating methods were used for the perovskite thin film preparation. In the one step method a solution of perovskite is spin-coated and during spin-coating anti solvent is dripped. In the two step method, the PbI\(_2\) thin film is spin-coated at first and subsequently the layer of methylammonium (MA) or formamidinium (FA) iodide is spin-coated on the top. Various combinations of the solvents were tested to get good film quality. Thin polymer and hybrid films were prepared either from blend solution or by multistep spin-coating of the layers. Photophysical properties of thin films were studied by means of UV-vis absorption and photoluminescence spectroscopies. The presented results will be discussed in relation to the composition and film preparation method using various solvents.

Further, the materials under study were tested as active layer in photovoltaic and light-emitting devices and their characteristics were measured.

**Keywords:** perovskite, conjugated polymers, photophysics, light-emitting devices, photovoltaic cells.

**Acknowledgement:** We thank the Czech Science Foundation for supporting this work with grant No. 18-14683J.

**References:**
Micropatterning strategies, which enable control over cell and tissue architecture, have emerged as powerful platforms for modelling tissue microenvironments at different scales and complexities. In this contribution we report preparation of complex surface structures of non-fouling polymer brushes and proteins and their characterization using advanced spectroscopic techniques and in cell adhesion experiments. Thin films of non-fouling polymer poly(oligoethylene glycol methyl ether methacrylate), poly(MeOEGMA), was prepared by surface-initiated atom transfer radical polymerization and patterned utilizing femto-second laser ablation. Immobilization of extra-cellular matrix proteins to patterned surface was performed and surface distribution of polymer and protein was investigated using X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE) and Fourier transform infra-red microscopy (FTIR).

Reference:
The extracellular and subcellular compartments are characterized by specific pH levels which can be considerably modified by pathophysiological states. Accordingly, when pH-stimuli responsive nano-assemblies are exposed to such milieus, they may respond by physicochemically changing their structure and/or surface charge. The structural changes of polymeric assemblies induced by environmental conditions can be exploited for the delivery of therapeutic drugs and genes into specific sites of action. In this framework, we highlight the potential use of pH-responsive block copolymers for the intracellular delivery of doxorubicin (Dox). Several (PHPMA-b-PDPA) diblock copolymers were synthesized by RAFT polymerization and characterized by 1H NMR and SEC. Self-assembled vesicular structures (also known as polymersomes) with a desirable size for cellular uptake produced by using the microfluidic technique (MF). They were further characterized by SLS, ELS and TEM. Dox was loaded in the PSomes and the cellular uptake and cytotoxicity were evaluated in EL4 lymphoma cancer cells. Due to promising results obtained in in vitro experiments, we decide to move forward and analyze the PSomes performance in in vivo experiments. A fluorescent dye (DBCO-Cyanine7) was covalently attached to the PSomes by click chemistry and the biodistribution of the PSomes performed in nude mice showed that the pH-responsive PSomes accumulated in the liver followed by the tumor. The biodistribution studies demonstrated the long blood circulation life time of the PSomes (~ 48h) if compared with the free-model fluorescent dye. In vivo antitumor efficacy was analyzed in mice bearing EL4 lymphoma tumor. The obtained results showed an improvement in the tumor shrink compared to the free-Dox. Side-effects characteristic to the therapeutic treatment with Dox such as hair loss and cardiotoxicity were improved with the PSomes.

Acknowledgement: The authors acknowledge the Czech Science Foundation (grant no. 17-09998S). L.J.C.A acknowledges the financial support from FAPESP (Grant 2017/11261-0 and 2016/23844-8).
DRUG-FREE E-SELECTIN-TARGETED THERAPEUTIC COPOLYMER FOR THE TREATMENT OF ALCOHOLIC LIVER DISEASE (ALD)

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Neutrophils infiltration is a prominent feature of alcoholic-liver disease and contributes to its severity.1,2 E-selectin is a cell adhesion molecule expressed on inflamed vascular endothelium and is a major regulator for leukocytes trafficking into inflamed tissues. Our group previously described the development of a “drug-free”, water-soluble N-(2-hydroxypropyl) methacrylamide (HPMA) copolymer displaying multiple copies of the high-affinity E-selectin binding peptide (Esbp) as a ligand for targeting E-selectin on inflamed vasculature.3,4 In this study we hypothesize that P-Esbp can be utilized to block the cell adhesion molecules interaction with neutrophils into the inflamed liver and control the extent of liver injury. C57BL/6 mice were subjected to chronic binge alcohol feeding diet for 10 days and received either saline, P-(Esbp) or P-(EsbpScrm) (i.p. 1mg, on day 10 and 11). Serum and liver samples were harvested for molecular biology, biochemistry and histology analysis. P-Esbp significantly attenuated the alcohol-feeding induced serum transaminase elevation and hepatic inflammation (mRNA expression of inflammatory cytokines and histological analysis). The scrambled version polymer conjugate P-(EsbpScrm) did not affect the transaminase elevation, confirming, once again, the attenuation of inflammation by blocking E-selectin-mediated activity.

References:
SUPERPARAMAGNETIC NANOPARTICLES: DESIGN FOR DRUG DELIVERY APPLICATIONS

V. Oleksa, H. Macková, V. Patsula, D. Horák

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic (www.imc.cas.cz)

Magnetic nanoparticles are being increasingly used in many biomedical applications, such as contrast agents in magnetic resonance imaging, heating mediators in hyperthermia, nanocarriers in targeted drug delivery systems, magnetofection, biosensors, transducers, cell separation and manipulation.

Aim of this work was to design a magnetically guided nanocarrier for delivery of anticancer drugs. Superparamagnetic iron oxide nanoparticles were prepared by thermal decomposition of Fe(III) oleate with oleic acid as a stabilizer, which allowed to produce uniform spherical nanoparticles with a controlled size. Typical hydrodynamic size from dynamic light scattering was $D_h = 22$ nm and polydispersity index PDI = 0.06. Moreover, the particles were characterized by transmission electron microscopy, FTIR spectroscopy, X-ray powder diffraction, and vibrating-sample magnetometer.

Because oleic acid-stabilized iron oxide particles were hydrophobic, a special polymer coating was needed to transfer them in water and ensure a long-term colloidal stability in physiological media. In this report, poly(\(N,N\)-dimethylacrylamide) (PDMA) was selected for modification of the particle surface due to its hydrophilicity, biocompatibility, non-immunogenicity, and last but not least, possibility to easily introduce reactive groups for subsequent attachment of biomolecules by copolymerization of \(N,N\)-dimethylacrylamide with a functional comonomer, i.e., \(N\)-acyroylglycin methylester. PDMA of different molecular weight was synthesized by the reversible addition-fragmentation chain-transfer (RAFT) polymerization in ethanol at 70 °C using 4,4’-azobis(4-cyanovaleric acid) (ACVA) as initiator and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) as chain transfer agent. The effect of DDMAT concentration, reaction time, and polymerization kinetic at different ACVA/DDMAT ratios was investigated. To achieve effective attachment of the polymer to the iron oxide surface, bisphosphonate anchoring group was introduced by Steglich esterification, yielding \(N\)-hydroxysuccinimide-activated PDMA, which was followed by reaction with sodium alendronate. Presence of phosphorus in the polymer was confirmed by \(^{31}\)P NMR. Hydrodynamic diameter of the particles increased from 198 to 247 nm with increasing molecular weight of the polymer. Incorporation of an anticancer drug in the polymer shell of the particles is in progress, as well as drug release and its effect on living cells.

Keywords: Magnetic nanoparticles, drug delivery, \(N,N\)-dimethylacrylamide, RAFT polymerization.

Acknowledgment: Support of the Czech Science Foundation (No. 17-04918S) is acknowledged.
NOVEL POLYMERIC DERIVATIVES OF BETULIN WITH ANTICANCER ACTIVITY

D. Niewolik\textsuperscript{a}, K. Jaszcza\textsuperscript{a,b}, B. Bednarczyk-Cwynar\textsuperscript{b}, P. Ruszkowski\textsuperscript{c}

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During the last years, there has been a growing interest in compounds obtained from renewable sources. Studies are carried out about the isolation of substances from plant extracts that may be used in such areas as the cosmetics and pharmaceutical industries. Such compounds can be used as ingredients of preparations, but may also be subjected to various modifications in order to obtain a new compounds, including polymers. One of these natural compounds is betulin.

Betulin, a lupine derivative, is a compound naturally occurring in nature. Both betulin and its derivatives have a broad spectrum of biological activity, including anti-inflammatory, antiviral and anti-cancer activity. Betulin derivatives are promising as new, potential therapeutic agents.\textsuperscript{1}

Disuccinate betulin (DBB) containing two carboxylic groups is excellent raw material to obtain polyanhydrides, a class of surface-degradable polymers. 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.\textsuperscript{2} Until now, there haven’t appeared reports regarding synthesis of polyanhydrides from betulin derivatives and thus there are no reports about the use of them in controlled drug delivery systems.

The aim of this work was the synthesis and characterization of a new polyanhydrides from disuccinate betulin, which can be used as biomaterials in controlled drug delivery systems. Polyanhydrides based on DBB were obtained by melt polycondensation with use of acetic anhydride. Under physiological conditions this polymers undergoes hydrolytic degradation to betulin disuccinate, whose biological activity is known and confirmed.

Keywords: betulin, polyanhydride, natural compound, cytotoxic activity.

References:
Nanomaterials are often used for drug delivery purposes since they can improve drug pharmacokinetics and biological activity. We focused this study on the synthesis and the study of physicochemical and biological properties of water-soluble \(\text{N-(2-hydroxypropyl)methacrylamide}\) (HPMA) copolymers and micellar poly(lactic-glycolic)acid-block-poly(HPMA) drug delivery systems in the field of inflammatory diseases, e.g., rheumatoid arthritis, which represent a serious problem in contemporary medicine. The studied polymer systems were evaluated for their suitability for effective delivery and stimuli-responsive activation of drugs. Fluorescently labeled polymer conjugates with the dexamethasone derivate bound via pH-sensitive hydrazone bond were accumulated in inflamed tissue in arthritic mice during the whole experiment (4 days) due to the ELVIS effect\(^1\)\(^2\). [Fig. 1] Presented results confirmed that described polymer systems are suitable as drug carriers and they have a great potential in effective delivery to inflammation.

**Fig. 1:** Biodistribution of HPMA linear copolymer with Cy 5.5 in the mice with acute arthritis in right ankle (red circle), time 24 hours

**Keywords:** HPMA, rheumatoid arthritis, biodistribution, fluorescent.

**Acknowledgement:** This work was supported by the Czech Science Foundation (grant No. 19-00956Y).

**References:**
CONDUCTING POLYMER COMPOSITE AEROGEL AS A BIFUNCTIONAL ADSORBENT FOR BOTH ANIONIC AND CATIONIC DYES


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Adsorption technology has been demonstrated to be a low-cost and highly efficient way to treat dye-containing wastewaters. However, the separation of powdered adsorbents from the aqueous solution has been the challenge for their practical application. In this work, a series of conducting polymer composites, i.e. polyaniline, poly(vinyl alcohol) and montmorillonite aerogels (PANI/PVAL/MMT-0, PANI/PVAL/MMT-20, PANI/PVAL/MMT-50) with different composition were synthesized. The obtained PANI/PVAL/MMT adsorbents were proved to exhibit easy separation characteristic. FT-IR spectroscopy, scanning and transmission electron microscopies, thermogravimetric analysis, X-ray diffraction, N₂ adsorption-desorption isotherms and zeta-potential measurements were performed to characterize PANI/PVAL/MMT adsorbents. The adsorption of three different dyes, i.e., Reactive Black 5, Methyl Orange and Safranin O onto the synthesized aerogels from aqueous solution were carried out at different solution pH and adsorbent dosage. Different kinetics models and isotherm models were adopted to study the adsorption behaviour and to determine the adsorption rates and capacities. The regeneration experiments were further investigated. Moreover, the possible mechanism of adsorption of these dyes was investigated and proposed. Results showed that PANI/PVAL/MMT-50 (Fig. 1) was a desirable bifunctional adsorbent for both anionic and cationic dyes, and combined with the easy separation property, it showed the great potential for the practical wastewater treatment.

Fig. 1. A typical SEM image and picture of PANI/PVAL/MMT-50 aerogel.

Keywords: polyaniline, montmorillonite, composites, aerogel, dye adsorption, easy separation.

Acknowledgement: The authors wish to thank the Czech Science Foundation (19-04859S) for the financial support. Dr. Wei Lyu participated in the UNESCO/IUPAC-sponsored Postgraduate Course in Polymer Science 2018/19.
RESISTIVE RANDOM ACCESS MEMORY BASED ON CONJUGATED POLYMERS MOLECULARLY DOPED WITH ORGANIC ACCEPTORS

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Non-volatile memory devices based on changes of electrical conductance with applied voltage were prepared as thin films of conjugated polymers mixed with low-molecular weight organic acceptors. Single and multilayer sandwich structures were studied. First, different diketopyrrolo-pyrrole (DPP) polymers and perylene derivatives were mixed at various ratios and cast as single layer structure sandwiched between ITO and Al electrodes. Such structure exhibited different electrical resistive switching under the application of electric field. Another multilayer sandwich structure was prepared as shown in Figure 1.c with top and bottom layers of composite of high-mobility donor-acceptor polymer, diketopyrrolo-pyrrole-dithienylthieleno[3,2-b]thiophene (DPP-DDT) and perylene-diimide separated by an intermediate layer of highly polar polymer dielectric, cyanoethylated polyvinyl alcohol, (CEPVA) blended with gold nanoparticles. Electrical bi-stability with high current ON/OFF ratio up to $10^3$, and high endurance non-volatile resistive changes with long retention time were observed. The highly polar dielectric CEPVA may enhance the accumulation of space charges in the boundaries between DPP-DDT and perylene domains and at interface between semiconductors and dielectrics domains. Stabilization of these charges by gold nano-particles and percolation through dielectric layer is responsible for better switching and memory effects in multilayer structure compared to the single layer system.

![Figure 1](image.png)

Keywords: Non-volatile memory, Conjugated polymers, Organic acceptors, Memory effect.

Acknowledgement: This work was supported by the Grant Agency of the Czech Republic, project No.17-03984S, and Technology Agency of the Czech Republic No. TE01020022.

References:
BEHAVIOR OF POLY [N-(3-(9H-CARBAZOL-9-YL) PROPYL) METHACRYLAMIDE] IN A RESISTIVE MEMORY DEVICE

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A resistive memory is a two-terminal nonlinear electronic device in which the information can be saved as low or high resistance state changed by applied voltage. In a special case of such a device, called memristor, the resistance is proportional to the charge that has passed through it.\(^1\) It has recently drawn the wide attention of scientists from various domains due to its extensive applications as nonvolatile memory in logic circuits and its ability to mimic neural synapsis in neuromorphic computing. Polymer materials have been considered as promising candidates for the implementation in memristor devices due to their low-cost, solution processability, mechanical characteristics and, tunable electrical properties.\(^2\)

In this work the poly [N-(3-(9H-carbazol-9-y1) propyl)methacrylamide] (PMMAK) has been applied in a memory device with ITO/PMMAK/Al structure. The memristor showed a reproducible bipolar resistive switching with high ON/OFF current ratio. Compared to poly (9-vinylcarbazole), which is known for its WORM memory behavior, the different polymer backbone and addition of the longer alkyl spacer between the chromophore and the main chain significantly improved the switching behavior, making the memory rewritable and having long persistence time. The device behavior was correlated with optical absorption and emission spectroscopy. We found the presence of vibrionic band in fluorescence spectra, and a slower decay in the excited state in transient optical absorption spectra. Both observations can be explained by better stabilization of charge transfer states due to more convenient mutual arrangement of the chromophores.

![Chemical structure of (a) poly [N-(3-(9H-carbazol-9-yl) propyl)methacrylamide] and (b) poly(9-vinylcarbazole).](image)

**Figure 1.** Chemical structure of (a) poly [N-(3-(9H-carbazol-9-yl) propyl)methacrylamide] and (b) poly(9-vinylcarbazole).

**Keywords:** Resistive memory, memristor, bipolar resistive switching, charge transport, organic electronics.

**Acknowledgement:** The authors wish to thank the GACR 17-03984S for the financial support.

**References:**
SOLID-STATE NMR SPECTROSCOPY OF POLYMERIC MATERIALS

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Nowadays, polymeric materials are widely used in different fields of life. Characterization of polymers and finding relations between their structure and properties are essential steps in development of new materials. Current work covers investigation of two kinds of polymeric materials and creation of a computational tool for polymorph selection from solid-state NMR data.

Firstly, the investigated materials are conductive polymers which have been actively used in applications such as polymer solar cells, organic light-emitting diodes, chemical sensors and organic semiconductors. Particularly polypyrrole attracts great interest of scientists due to its good thermal stability, electrical conductivity and environmental stability. However, relation between structure and properties of polypyrrole is still unclear. It was previously reported that low-conducting neutral form of polypyrrole is characterized predominantly by aromatic structure while high-conducting doped form is characterized by presence of quinoid structure.1 From previous solid-state NMR studies of polypyrroles it was observed that recording of high-quality $^{13}$C NMR spectra is complicated, due to their conductivity.1,2 In this work series, polypyrrole samples with different conductivity were investigated and correlation between NMR parameters and conductivity of polypyrrole was found.

Secondly, the structural arrangement and subsequent transformation of silicon oxycarbide glasses were mapped. Silicon oxycarbide is known for its good mechanical properties and thermos-oxidation resistance.3 One of the ways to synthesize silicon oxycarbide is controlled pyrolysis of polysiloxanes. Therefore, structure changes of the precursor during pyrolysis in order to find out its influence on final product were investigated. As result of $^{13}$C and $^{29}$Si CP/MAS NMR experiments, NMR spectra of series of the samples based on poly(methylsiloxane) and poly[methyl(phenyl)siloxane] precursors were obtained.

Last part of the presented work is devoted to polymorph selection in solid-state NMR. In case when the solid sample contains several polymorphs, resolving and determination of their structure by solid-state NMR can be problematic. A number of structural models predicted using quantum-chemical calculations is compared with experimental NMR data and the most appropriate structural model is selected from the calculated dataset. To automate this comparison procedure, a program with graphical user interface was created.

Keywords: solid-state NMR, polypyrrole, silicon oxycarbide, polymorph selection.

References:
3D VISUALIZATION AND COMPUTER-AIDED RECONSTRUCTION OF HYDROGEL SCAFFOLDS

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Synthetic water-swelling hydrogels are known as excellent candidates for cell tissue engineering for their biocompatible and mechanically matching properties. In biomedicine and tissue engineering, it is important to fabricate complex spatial geometries involving 3D system of channels-pores in the hydrogel that guide the cell growth within the scaffold. The architecture of pores, their connectivity, shape and size should be adjusted to the specific cell type requirements. Therefore, it is important to visualize and quantify the fabricated 3D scaffold features. In this respect, gel visualization in its equilibrium swollen state in water has been carried out through the method of laser scanning confocal microscopy (LSCM) enabled by covalently incorporated fluorescein dye. For each gel sample, hundreds of x-y planes were scanned along the z-axis. The acquired z-stacks were processed for 3D reconstruction including data deconvolution to correct the systematic error of blur. The softwares Materialise Mimics®, Fiji ImageJ, and Avizo were used for data reconstruction, cf. example of reconstructed macroporous hydrogel on Figure 1. The number of voxels of the gel phase versus number of voxels of diluent (pore volume) was quantified, and the pores connectivity evaluated. The developed method of 3D hydrogel/pores volume phase visualization will be used to characterize the structure of hydrogel scaffolds precisely designed and made by the 3D printing of UV-reactive hydrogel ink based on droplet-deposition or extrusion technique.

Figure 1. Hydrogel with connected pores made from poly(2-hydroxyethylmethacrylate). The gel phase structure was formed by cross-linking induced phase separation; sample visualized by – from left to right: environmental SEM, LSCM, 3D reconstruction of 241 z-stacks obtained by LSCM in Materialise Mimics®.

Keywords: Hydrogel scaffolds; 3D reconstruction; Visualization; Porosity.

Acknowledgement: Czech Science Foundation, Project No.17-08531S; Department of Morphology of IMC.
PHOTOCHEMICALLY INDUCED COPPER MEDIATED ATOM TRANSFER RADICAL POLYMERIZATION OF TULIPALIN A

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Compared to other initiating systems of atom transfer radical polymerization (ATRP), the photoinduced one (photoATRP) is one of the most attractive. It is environmentally benign due to avoiding of additional chemicals, the low catalyst concentrations and mild radiation sources with excellent control over polymerization. Furthermore, the reaction can be stopped and recommenced simply by switching on or off the radiation source.\(^1\) PhotoATRP system was reported for the first time by Yagci and co-workers.\(^2\) Mosnáček and co-workers reported recently the photoinduced ATRP of both acrylic and methacrylic monomers without photoinitiators and with ppm amounts of Cu catalysts.\(^3,4\) He also contributed for further optimization of photoATRP to be conducted in presence of limited amount of oxygen, what is very important factor from the industrial point of view.\(^4,6\)

As in all other ATRP methods, the rate of polymerization in photoATRP depends also on the rate of radical generation, i.e. rate of reduction of Cu\(^{II}\). This can be adjusted by varying light intensity, irradiation wavelength, and the concentration and ratio of Cu and ligand.\(^7\) It is worth mentioning that the reaction can proceed fast and with no induction period even when excess of high expensive ligands is partially replaced by cheap tertiary amines.\(^6\)

Tulipalin A (α-methylene-γ-butyrolactone - MBL) is a naturally occurring monomer, which can be extracted from tulips. With a two polymerization sites, MBL has successfully been co/polymerized using different polymerization techniques including ATRP.\(^8\) However, there is no report on polymerization using ATRP techniques using low catalyst concentrations so far. Here we report the first preparation of a well-defined homopolymer of MBL using photoATRP.

Keywords: photopolymerization, functional polymer, well-defined polymer, renewable monomer.

Acknowledgement: This work was supported by projects APVV-15-0545 and VEGA 2/0161/17.

References:
BIODEGRADABLE POLYURETHANE FOAMS WITH DIFFERENT MORPHOLOGY AND THEIR EFFECT ON ENVIRONMENT

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Major priority in waste management is decreasing the amount of plastic waste and prevention of its accumulation, according to the European Directive 2008/98 / EC of the European Parliament and of the Council on waste and the Waste Act No. 185/2001 Coll., as amended. The use of biodegradable plastics could be a suitable route to implementing this strategy. Nowadays, biodegradable cellular polyurethanes (PURs) with open micropores (100–1000 μm)¹ are highly requested for new environmental technologies such as biofilters, carriers of microorganisms, odorants and vapor sorbents, capture of catalysts, etc. For these applications it is important that PURs are not toxic and capable of decomposing in the environment, both via abiotic (hydrolysis, photodegradation) and biotic (soil microorganisms) pathways².

In this work, various polyester polyols based on succinic or adipic acids and glycols with different polarity were first synthesized and then used for preparation of PUR foams. Different types of surfactants and fillers (clays, starch, etc.) were added to PUR formulation resulting in different PUR foam porosity and cellular structure. The hydrolytic cleavage of ester bonds plays a key role in microbial attack, while the glycolytic segment of PUR foam is responsible for hydrophilicity.

Then, the selected PUR foams were subjected to accelerated aging (abiotical way) and biological deterioration in soil. The PUR foam’s biodegradability was tested respirometrically according to the ASTM D 5988 under laboratory conditions. The progress of PURs degradation was monitored gravimetrically and using FTIR spectroscopy, which evidenced the hydrolysis of both esters and urethane bonds.

Ecotoxicological tests were conducted on water extracts from different phases of abiotic decomposition. Organisms Dafnia magna, Sinapis alba and Desmodesmus subspicatus were used for analysis which provided LC₅₀ and LOAC.

Keywords: Biodegradability, polyurethane foams, ecotoxicology.

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References:
POLYURETHANES WITH INTEGRATED INORGANIC/ORGANIC BLOCKS

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Waterborne polyurethane dispersions (PUD) based on polycarbonate diol, 2,2-bis(hydroxymethyl)propionic acid, 1,6-diisocyanatehexane and triethylamine were synthetized. The molar ratio isocyanate-to-hydroxyl\textsubscript{total} varied from 1.05 to 1.5. The residual isocyanate reacted subsequently with water during the phase inversion step so that PUDs with different degree of branching/crosslinking were synthesized. The given excess of NCO groups enabled to establish the correlations between synthesis parameters and functional properties of films prepared from PUDs in absence or presence of inorganic building units. Three series were studied: pure polyurethane (PU) films and PU nanocomposite films prepared in the presence either of 0.5 wt\% of Cloisite Na\textsuperscript{+} (montmorillonite, MNa) or 5 wt\% of colloidal silica, SiO\textsubscript{2}. Tensile tests revealed that the samples with 40 mol \% excess of isocyanate had the highest value of tensile stress and toughness while films with 30 mol \% NCO excess had the highest value of elongation at break. The morphology studies of film surfaces show that the fibril-like structures were detected on pure PU films and on films containing silica nanoparticles (Fig. 1); MNa presence suppressed fibril formation. ss-NMR spectroscopy did not indicate any significant differences in structure and segmental dynamics of prepared systems with or without any filler, that corresponds to FTIR results. However, the differences of sample properties were found on supramolecular and higher levels.

![Figure 1. AFM-SEM micrographs of films made from PUD prepared with 40 mol \% NCO excess, a) without any filler and b) with SiO\textsubscript{2}](image)

Keywords: waterborne polyurethane dispersion, film, silica, montmorillonite.

Acknowledgement: Financial support of Czech Science Foundation (18-03932S), UNESCO and IUPAC is appreciated.
ION EXCHANGE MEMBRANES FOR APPLICATION IN FUEL CELLS

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Polymer ion exchange membranes are materials for applications in energy conversion (fuel cells, water electrolyzers, electrodialysis, etc.), which have fixed charges in the polymeric chain. Sulfonated and quaternized polymers have been considered as an adequate alternative to perfluorinated polymers for the production of ion exchange membranes for fuel cells. Currently, Nafion is the most widely used commercial perfluorinated polymer for such applications. However, the high cost and the limit in the operating temperature are serious problems that this type of polymer has presented. Alternative methods to obtain ion exchange membranes are gaining attention compared to conventional methods, due to some problems that occur with hard acids as in the cases of the direct sulfonation of aromatic polymers.

In this work, there were synthesized chloromethylated polysulfone and chloromethylated polySEBS (polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene) by the reaction with dimethoxymethane (formaldehyde precursor), ZnCl₂ (catalyst), and silicon tetrachloride (chlorinating agent).¹ Chloromethylated polymers were dissolved in organic solvents and cast on Teflon plate to obtain dense membranes by the method of solvent evaporation. In addition, chloromethylated groups in the membranes were chemically modified by different routes to obtain sulfonated membranes and quaternized membranes. The prepared membranes were characterized by measuring ion conductivity, ion exchange capacity, water uptake and others. Special attention was paid to oxidation stability test of prepared membranes.

Keywords: Ion exchange membranes, polySEBS, polysulfone, sulfonated membranes, quaternized membranes, ion conductivity, oxidation stability test.

Acknowledgement: The financial support of this research received from the Grant Agency of the Czech Republic under the project No. 16-20728S is highly appreciated.

References:
STUDY OF BEHAVIOR OF HOFFMEISTER SERIES ANIONS ON ETHYLENE GLYCOL BASED POLYMER BRUSHES

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Ions of the Hofmeister series have strong influence on the solubility of proteins, the aggregation behavior of block copolymers, the physicochemical properties of charged end-tethered polymer chains, etc. Investigation of interphase polymer behavior is required to obtain well-controlled polymeric material.

In this report we focus on probing the influence of the of F\(^-\), Cl\(^-\) and SCN\(^-\) anions from the Hofmeister series on the physico-chemical properties of ethylene glycol based polymer chains using parallel measurement of spectroscopic ellipsometry (SE) and quartz crystal microbalance with dissipation monitoring (QCM-D). 2-hydroxyethyl methacrylate, oligo(ethylene glycol) methacrylate and oligo(ethylene glycol) methyl ether methacrylate polymer brushes were synthesized from the activated silicon and gold surfaces via surface initiated atom transfer radical polymerization (SI-ATRP). Different in situ and ex situ surface sensitive techniques, such as grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GAATRFTIR), XPS, etc., have been used to probe the surface parameters of the “grafted from-“ polymer chains and correlate them to the QCM-D and SE findings.

The exposure of the brushes to solutions of kosmotrope F\(^-\) anions with high ionic strengths induced a collapse of the polymer brushes. At the same time, the exposure to solutions of chaotrope SCN\(^-\) anions induced strong swelling. The collapse and swelling of the polymer brushes as a function of the ionic strength of the kosmotrope and chaotrope solutions was further proved by modeling the viscoelastic properties of the polymer brush films.

![Figure 1. Representation of specific ion effect on polymer brushes](image)

**Keywords:** polymer brushes, ATRP, QCM-D, specific ion effect, modeling of QCM-D data.
POLYPYRROLE-NANOFIBRILLATED CELLULOSE CRYOGELS: SYNTHESIS AND APPLICATION

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Nowadays soft electronics are in high demand, among the different forms of conducting materials; conducting gels have become good candidates. They provide both the electric conductivity and mechanical flexibility which are prerequisite for such applications. In this work, one step facile preparation of polypyrrole–nanofibrillated cellulose (PPy–NFC) cryogels is reported. PPy–NFC was prepared via an in situ oxidative polymerization of pyrrole with iron(III) chloride in the presence of NFC as the biotemplate. The mechanical properties of cryogels improved by increasing the NFC content from 0.1 to 2 wt.%. The tensile modulus with the value 0.347 MPa was achieved at the concentration of 2 wt.% of NFC. SEM micrographs show the formation of three-dimensional network structure (Fig.1) with different pore sizes according to the NFC content. PPy works as an adhesive to fix the cellulose nanofibers together creating low density, uniform, flexible, compressible and hydrophilic substrates with high specific surface area (46–67 m²/g). All the compressed pellets of all PPy–NFC samples showed higher conductivity than the conventional PPy. The highest conductivity was achieved in the sample with 0.7 wt.% of NFC with the value of 31 S cm⁻¹. Moreover, this cryogels showed the ability to adsorb heavy metals from solutions, based on the high specific surface area and the ion exchange properties.

Fig. 1. Polypyrrole-nanofibrillated cellulose cryogels prepared in a plastic syringe as a mold, and the SEM micrograph of a sample containing 0.7 wt.% of NFC.

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T-CELL MEDIATED DRUG DELIVERY ACROSS THE BLOOD-BRAIN BARRIER

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Cell-mediated drug delivery is a potential method to enhance drug targeting by taking advantage of intrinsic cellular properties. One example of a challenging target for drug delivery is the central nervous system (CNS), which is protected by the blood-brain barrier (BBB). Certain circulating immune cell subsets including effector/memory T cells are able to cross the BBB also in the absence of neuroinflammation. Modification of the surface of these T cells with drug-loaded polymer nanocarriers thus presents a potential strategy to enhance the delivery of drugs into the CNS.

This study investigates the immobilization of 200 nm sized biodegradable fluorescent polymer nanoparticles using different covalent and non-covalent immobilization methods on the surface of human Jurkat and mouse CD4+ effector/memory T cells. Cell surface conjugation of the nanoparticles and the influence on cell viability and proliferation was monitored by flow cytometry. Using confocal microscopy, the position, distribution and number of particles on the cell surface was determined. We found that T-cell surface coupling of nanoparticles depends on the number of nanoparticles added to the cells and the most efficient strategy to attach nanoparticles was via ligand-receptor interactions (lectin – sialic acid and biotin – NeutrAvidin). Furthermore, T cells can be decorated with up to 184 ± 56 nanoparticles per cell without significantly affecting cell viability. The nanoparticle decorated T cells were investigated for their ability to cross an in vitro mouse BBB model under static conditions in a two-chamber assay. Decorating the cells with nanoparticles does not affect their ability to bind ICAM-1 (a protein involved in the transmigration process) or to cross a biological barrier. We observed cells coated with nanoparticles migrate across the model barrier. However, migration led to a loss of nanoparticles.

Keywords: T-Cell mediated drug delivery, cell surface conjugation, nanoparticles, PEGylation, blood-brain barrier, Jurkat cells, CD4+ TEM cells, neuroinflammation, transendothelial migration.

Acknowledgement: Swiss National Science Foundation.
CONDUCTING CRYOGELS BASED ON ANILINE AND M-PHENYLENEDIAMINE WITH CONTROLLABLE CHARACTERISTICS


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Polyaniline-based cryogels are macroporous materials which combine conductivity and physico-chemical properties of the conducting polymer with mechanical properties of the polymer stabilizer. They are prepared by oxidative cryopolymerization in a frozen medium. Depending on the application requirements, morphology, conductivity and mechanical properties of the material can be tailored by tuning the polymerization conditions and composition of the reaction medium.

In the present work, conducting copolymer cryogels of aniline and m-phenylenediamine stabilized by poly(vinyl alcohol) (Figure 1) were synthesized using different initial freezing temperatures and total comonomer concentrations. It was shown that increase of initial freezing temperature from –78°C to –20°C led to decrease of pore sizes in resulting cryogels. This change also induced improvement of mechanical integrity of the composites and increase of their tensile modulus. Decrease of total comonomer concentration from 0.8 M to 0.2 M was found to have an opposite effect: considerably larger pores and lower mechanical stability of the final materials. Studying of the cryogels by vibrational spectroscopy showed that in all used experimental conditions partially deprotonated polyaniline was formed. Conductivity of all the materials remained at ~10^{-3} S cm^{-1}.

Figure 1. Scanning electron microscopy images of poly(aniline-co-m-phenylenediamine)/poly(vinyl alcohol) cryogels.

Keywords: cryogels, polyaniline, conductivity, morphology, mechanical properties.

Acknowledgement: The authors wish to thank the Czech Science Foundation (18-04669S) for the financial support.
ELUCIDATING THE ROLE OF HYDROGEN-BOND INTERACTIONS ON PHYSICOCHEMICAL PROPERTIES OF PEDOT


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Among electronically conducting polymers, there is a considerable interest in using poly (3,4-ethylenedioxythiophene) (PEDOT) because of its low oxidation potential, high stability in ambient environments, mechanical flexibility and stable oxidized form. The physicochemical properties of PEDOT depend on several factors such as: 1) method of preparation (chemical or electrochemical), 2) temperature, 3) concentration, 4) additives and 5) post-treatment.

It has been shown that polymers with basic nitrogen or sulphur atoms offer the possibility of protonation or alkylation of the lone pair as a way of modifying their properties. Recently, it has been shown that protonation of the pyridyl nitrogen has an important structural effect: formation of intermolecular hydrogen bonding between the adjacent polymer chain leads to planarization of the polymer backbone, and the consequence the red shifts of both the optical absorption and emission spectra are observed.

In this work, we study the effect of structural constraints, induced by covalent cross-links, on the folding of a PEDOT polymer chain via hydrogen-bonding interactions in the present of formic acid. A combination of UV-Vis and NIR absorption, Raman spectroscopy, electron spin resonance and X-ray photoemission spectroscopies were employed to understand the effect of the structural constraints provided by hydrogen bond on the physicochemical behavior of PEDOT polymer.

Keywords: poly(3,4-ethylenedioxythiophene), hydrogen-bonding.

Acknowledgement: We acknowledge Czech Grand Agency (grant number: 19-04859S).

References:
SYNTHESES AND ELECTRICAL PROPERTIES OF POLY(P-PHENYLENEDIAMINE)/MAGHEMITE COMPOSITES

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There has been a growing interest in conducting polymers composites with maghemite filler.¹ Such materials possess both electrical properties of polymers and magnetic properties of iron-oxide particles which extends their applicability in a wider range of applications. Although poly(p-phenylenediamine) has only relatively low DC conductivity ≈10⁻⁹ S cm⁻¹ or lower at room temperature,² it is frequently exploited in electrocatalysis, electrorheology, and in sensors. We synthesized poly(p-phenylenediamine)/maghemite composites via simple two steps procedure. First, γ-Fe₂O₃ nanoparticles were prepared by co-precipitation of Fe³⁺ and Fe²⁺ salts followed by oxidation of Fe₃O₄ with sodium hypochlorite. Second, p-phenylenediamine dihydrochloride was polymerized in-situ with ammonium peroxydisulfate in the presence of γ-Fe₂O₃ nanoparticles in aqueous solution. Obtained composites were characterized by electron scanning microscopy, differential scanning calorimetry, thermogravimetric analysis, magnetic and DC conductivity measurements. After preparation the composite with 50 wt.% showed conductivity around 10⁻¹¹ S cm⁻¹, only slightly lower than the pure polymer, but after annealing at 160 °C the value surprisingly increased one order of magnitude and the broadband impedance spectroscopy showed that the relaxation frequency of dipole polarization follows Vogel-Fulcher-Tammann (VFT) law.

Keywords: poly(p-phenylenediamine), maghemite, composite, conductivity.

Acknowledgement: The authors wish to thank the Czech Science Foundation (18-04669S) and TACR TE01010022 for the financial support.

References:
The f-MLF compounds are very famous for the development of therapeutic agents because they play a very important role in host defense and inflammation. Nowadays, the challenge is to create some analogues to develop some active principle. These compounds are also used a lot in NMR spectroscopy but the structure of some samples like f-MLF-OCH3 is always unknown. In this report we are going to try to determine this structure by using the NMR crystallography method. The determination of structure by ssNMR crystallography still remains a good challenge because this technique is not well developed. By using basics of ssNMR combined with some computing calculation we hope that we could be able to determine the correct structure of the f-MLF-OCH3 compound. The aim of this project was in a first hand to improve our skills in the field of NMR crystallography and in a second hand to precisely determine the crystal structure of this tripeptide which is used a lot in some project. To probe this structure we are going to process some simple 1H, 13C and 15N ssNMR spectra in one dimension and also some correlation spectra in two dimensions. The results would be comparing with the calculated one from a computed structure prediction.
SCAVENGING OF REACTIVE OXYGEN SPECIES BY PHENOLIC COMPOUND-MODIFIED IRON OXIDE NANOPARTICLES

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Iron oxide nanoparticles (IONs) are widely investigated in terms of their application in various biomedical fields as they can be remotely controlled by an external magnetic field and easily surface-modified to increase their stability under physiological conditions or incorporate diverse biological moieties, including drugs, antibodies, etc.\textsuperscript{1}

In this study, we modified IONs via a layer-by-layer technique with heparin and chitosan conjugated with phenolic compounds, namely gallic acid, hydroquinone, and phloroglucinol, to prepare materials with antioxidant properties that can serve as effective scavengers of reactive oxygen species (ROS) and consequently reduce oxidative stress that is known to negatively influence cellular functions leading to many disorders, such as Alzheimer’s disease, cancer, and diabetes.\textsuperscript{2}

The ION modification was confirmed using thermogravimetric and elemental analysis and dynamic light scattering. The ability of IONs to scavenge ROS was determined using 2,2-diphenyl-1-picrylhydrazyl and total radical-trapping antioxidant potential assay. Furthermore, the cytotoxicity and efficacy to reduce oxidative stress was investigated \textit{in vitro} on murine fibrosarcoma (L-929), human glioblastoma cells (LN-229), and polymorphonuclear cells (PNM) isolated from the human whole blood.

Our results showed that antioxidant properties and cytotoxicity of the nanoparticles depended on their concentration, surface modification, and type of cells. The particle concentration of 100 μg/ml did not affect significantly viability of the L-929 and LN-929 cells, however, it had a visible impact on PNM cells, for which the lowest viability reached ∼60%. In L-929 and LN-929 cells, the ability of phenolic compound-modified IONs to scavenge ROS was significantly higher compared to neat and heparin-coated nanoparticles, however, nanoparticles containing gallic acid provided only a small advantage. In PNM cells, gallic acid-modified nanoparticles showed the highest inhibition of PMN cell oxidative burst amid investigated particles.

Presented results proved that IONs coated with polymers modified with phenolic compounds can be a useful tool to suppress an oxidative stress and its damaging effects.

\textbf{Keywords:} magnetic nanoparticles, phenolic compounds, chitosan, reactive oxygen species.

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\textbf{References:}