

XII. Czech - Slovak Conference

Polymers

3 - 6 / 10 / 2022

Třešť Chateau

BOOK OF ABSTRACTS



INSTITUTE OF
MACROMOLECULAR
CHEMISTRY
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XII. Czech – Slovak Conference

Polymers 2022

3 – 6 October 2022, Třešť Chateau

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Dear colleagues and friends,



welcome to the XII. Czech-Slovak conference Polymers 2022 at the chateau Třešť in the period October 3-6, 2022! We are glad that our meeting can be held in the newly reconstructed building of the beautiful chateau.

The scope of our traditional conference covers various aspects of polymer science including polymer synthesis, material engineering, biomedical or industrial applications, etc. Every two years, the chemists and physicists from both countries have a unique opportunity to share knowledge, learn new things, and get inspiration. Moreover, after the last two years of only online talks, it is especially important to meet old and new colleagues and create new informal work contacts or even possibly establish new collaborations.

For the first time, the official conference language is only English. Thus, the conference is now open to colleagues originally coming from foreign countries, and we hope their presence will enrich the quality of the meeting.

The conference offers not only a variety of lectures or poster contributions but also plenty of time for networking or meeting colleagues and friends.

Enjoy the conference!

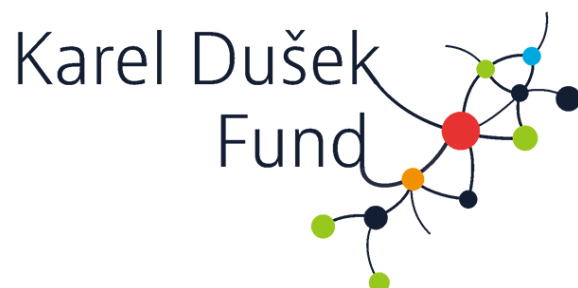
Petr Chytil

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We thank for the support:



Best presentation award is supported by:



Třešť Chateau

Třešť Chateau is a neo-renaissance building located near the center of the town Třešť in the Jihlava district. Nowadays, it serves as a conference center. Many important conferences and events have taken place here, for example, meetings of the academies of sciences of the Visegrád Four or regular meetings with the Slovak Academy of Sciences.



Its history began in 1513 when a fortress was built there. In the second half of the 16th century, the fortress was rebuilt into a Renaissance castle. Later it was reconstructed several times, firstly in baroque style, and finally in a neo-renaissance style in 1860. There were many owners during its long history. Since 1973 it has been

a cultural monument, and since 1984 it has belonged to the Czech Academy of Sciences. The last large-scale reconstruction of the chateau and a vast park was finished this year, and it is open to the public again.

The chateau is somehow connected with the famous writer Franz Kafka, who stayed 1900–1907 with his uncle during the summer holidays. The majestic building of the chateau could possibly inspire him when writing the novel *The Castle*. However, this hypothesis has neither been confirmed nor refuted.



Thanks to the cooperation of the Czech Geological Survey and geologists from the Czech Academy of Sciences, a completely new geological educational trail has been opened in the adjacent park.

The exhibition with the subtitle “Renaissance region against the current of time” provides a summary insight into the varied geological history not only of the local region but of the entire Czech Republic.

(Adapted from www.avcr.cz)

Conference Programme

Monday, 3 October 2022

17:00 – 18:30

Registration

19:00

Welcome dinner

Tuesday, 4 October 2022

9:20 – 9:30

OPENING

Jiří Kotek, Petr Chytil

Chaired by: Jiří Kotek

9:30 – 9:50

L-01

Zdeněk Starý

Wall slip and instabilities in capillary flow of lubricated polyethylene melt

9:50 – 10:10

L-02

Yaryna Soyka

Preparation and properties of composites with hybrid nanofillers

10:10 – 10:30

L-03

Zhejing Cai

Sustainable thermoplastic material based on potato starch and natural rubber

10:30 – 11:00

Coffee break

Chaired by: Hynek Beneš

11:00 – 11:20

L-04

Zuzana Benková

Adsorption of mono-peptides onto carbon nanotubes grafted with poly(ethylene oxide) chains. molecular dynamics study

11:20 – 11:40

L-05

Abolfazl Heydari

Modification of chitosan by permanently charged cationic and anionic moieties: An interesting science behind at glance simple approaches

11:40 – 12:10

L-06

Pavel Izák

A new chiral membranes for racemix mixture separation

12:10 – 12:30

L-07

Stanislav Kukla

Big science with small footprint

12:30 – 14:00

Lunch

Chaired by: Igor Lacík

- 14:00 – 14:35 IL-01
Robin Hutchinson
Efficient synthesis of acrylic block copolymers in a semi-batch process
- 14:35 – 14:55 L-08
Sachin Gupta
Cu(0)-RDRP of 2-hydroxyethyl methacrylate in a non-polar solvent: Rapid synthesis of well-defined, high-molecular weight (co)polymers
- 14:55 – 15:15 L-09
Vladimír Raus
Adducts of trichloroacetyl isocyanate: A new class of multifunctional initiators for copper-mediated RDRP
- 15:15 – 15:35 L-10
Rafal Poreba
Antifouling surfaces via interface-mediated photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFZ) polymerization
- 15:35 – 15:55 L-32
Dušan Račko
Channels with helical modulation display stereosensitivity for chiral superstructures

15:55 – 18:00 **Social afternoon**

18:00 – 19:30 **Barbecue**

19:30 – 22:00 **POSTER SESSION**

Wednesday, 5 October 2022

Chaired by: Zdeněk Starý

9:30 – 9:50 L-11

Josef Jůza

Polymer blends compatibilization using copolymers: modification of simple estimation methods

9:50 – 10:10 L-12

Monika Hittlová

Influence of waste rubber powder (WRP) activation temperature on the behavior of WRP-modified rubber matrix

10:10 – 10:30 L-13

Marwa Rebei

Ionic liquid-induced formation of bio-sourced epoxy network

10:30 – 11:00

Coffee break

Chaired by: Jan Sedláček

11:00 – 11:20 L-14

Jan Merna

Special polyolefins by chain walking catalysts

11:20 – 11:40 L-15

Bogdana Bashta

Porous hyper-cross-linked polymers prepared via templating method

11:40 – 12:00 L-16

Vojtěch Musil

Chain walking polyethylene as impact strength modifier of polystyrene

12:00 – 12:20 L-17

Alena Hašková

Porous ionic hyper-cross-linked polyacetylenes with chiral and achiral segments

12:20 – 14:00

Lunch

Chaired by: Zuzana Benková

- 14:00 – 14:20 L-18
Hynek Beneš
Sustainable polyitaconic acid / nanoclay hydrogels
- 14:20 – 14:40 L-19
Aakash Sharma
Polyurea protective coatings with fast drying times. Understanding of crosslinking film formation
- 14:40 – 15:00 L-20
Miroslava Dušková-Smrčková
Hydrogels may turn stimuli-responsive under strain
- 15:00 – 15:20 L-21
Stepan Podzimek
Molecular structure of recycled polymers by size exclusion chromatography and advanced detectors

15:20 – 15:50 *Coffee break*

Chaired by: Michal Pechar

- 15:50 – 16:10 L-22
Juraj Kronek
New gradient copolymers based on aliphatic and aromatic 2-oxazolines for photodynamic therapy
- 16:10 – 16:30 L-23
Faeze Dorchei
Post-modification of multicomponent PMCG microcapsules with polyelectrolytes: Impact on microcapsule characteristics and biocompatibility
- 16:30 – 16:50 L-24
Martin Hrubý
Thermo-, pH- and reactive oxygen species-responsive polymer contrast agents for ^{19}F magnetic resonance imaging
- 16:50 – 17:10 L-25
Ladislav Androvič
Novel biocompatible polymer probes for dual ^{31}P and ^{19}F magnetic resonance imaging

19:00 **Conference dinner**

Thursday, 6 October 2022

Chaired by: Juraj Kronek

9:30 – 9:50 L-26

Rachel Yerushalmi-Rozen

Modification of acid-base equilibria of weak polyelectrolytes in complex fluids

9:50 – 10:10 L-27

Volodymyr Lobaz

Interactions of proteins with synthetic polymers

10:10 – 10:30 L-28

Jaroslav Kolejka

Modern methods of thermal and mechanical analysis of polymers

10:30 – 11:00

Coffee break

Chaired by: Jan Merna

11:00 – 11:20 L-29

Jana Machotová

Water resistance of latex coatings: Effect of crosslinking, fluorinated comonomer, and polymerizable surfactant

11:20 – 11:40 L-30

Vojtěch Jašek

Synthesis of novel bio source polymerizable coating precursors based on depolymerized poly lactic acid (PLA)

11:40 – 12:00 L-31

Ondřej Štrympl

Laurate modified low molar mass sodium hyaluronan association and solubilization efficiency in aqueous media

12:00

CLOSING OF THE CONFERENCE

12:30

Lunch

List of Posters

- P-01 **R. Balogh**, A. Eckstein, M. Danko, K. Tokár
Synthesis and spectral study of asymmetric thiazolo[5,4-*d*]thiazole based molecules with 1,3,4-oxadiazole linker for electronic application
- P-02 **A. Braunová**, M. Kaňa, M. Šírová, J. Kudláčková, L. Kostka, T. Etrych
Amphiphilic block copolymers as nanomedicines for efficient treatment of resistant tumors
- P-03 **M. Dizon**, J. Kollár, J. Mosnáček, M. Danko
Synthesis of novel bio-based polymer gels and the evaluation of their swelling performance
- P-04 **O. Gotkiewicz**, O. Kočková, M. Kirpluks, U. Cabulis, H. Beneš
Low-density semi-rigid polyurethane foams based on bio-based polyols
- P-05 **A. Hlukhaniuk**, V. Patsula, J. Hodan, A. Brož, D. Horák, M. Świątek
Modified magnetic polymer composites for biomedical applications
- P-06 **M. Majerčíková**, S. Brandner, P. Strasser, I. Teasdale, Z. Kroneková, J. Kronek
Synthesis of hybrid polymer materials from poly(2-oxazoline)s and polyphosphazenes
- P-07 **M. Moskvín**, V. Huntošová, I. Marková, H. Malínská, D. Horák
PEGylated iron/cerium oxide nanoparticles with magnetic and antioxidant properties
- P-08 **S. Natour**, V. Gajdošová, Z. Morávková, M. Dušková-Smrčková
Dwelling into polyurea ambient-cure protective coatings: Characterization of film forming properties and depth-dependent curing
- P-09 **M. Nevoralová**, S. Bujok, R. Konefał, M. Konefał, H. Beneš, K. Mielczarek, S. Bednarz
The influence of clay dispersion pH on the mechanical properties of the nanocomposite hydrogels
- P-10 **M. Pechar**, R. Pola, R. Laga, V. Král, M. Fábry, O. Vaněk
Polymer therapeutics and diagnostics targeted with recombinant antibody fragments
- P-11 **S. Pytlíková**, P. Chytil, M. Pechar, K. Kotalík, T. Etrych
Hydrophilic polymer-pirarubicin conjugates for cancer treatment
- P-12 **J. Uříčář**, J. Brožek, J. Minář
Carbon black composites via stereolithography
- P-13 **T. Vasylshyn**, V. Patsula, D. Horák
Poly(2,3-dihydroxypropyl methacrylate)-coated upconverting nanoparticles for biomedical applications
- P-14 **M. Vragovic**, V. Sincari, M. Hrubý, A. Jäger, E. Jäger
pH-responsive giant unilamellar vesicles

Notes:

Abstracts of Lectures

IL-01

EFFICIENT SYNTHESIS OF ACRYLIC BLOCK COPOLYMERS IN A SEMI-BATCH PROCESS

H. M. Deacon, R. A. Hutchinson

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Starved-feed semi-batch radical polymerization is widely used commercially to convert inexpensive monomers to functionalized acrylic random copolymers for coatings and adhesive applications. However, the short chain lifetimes do not allow the synthesis of block copolymer structures that provide superior performance for some applications. Thus, reversible deactivation radical polymerization has attracted considerable academic and industrial interest as a synthetic tool to produce value-added materials. However, these novel chemistries still require engineering solutions for successful commercial application. This presentation describes the adaptation of the semi-batch operating strategy to synthesize copolymers with structured architectures, thus producing higher-value block copolymers using existing infrastructure.

A process for the well-controlled growth of acrylates by Cu-mediated polymerization has been developed, using poly(acrylate) macroinitiator synthesized continuously in a copper tubular reactor. The macroinitiator solution can be stored without purification and subsequently chain-extended in a semi-batch reactor system to >90% conversion in 4 h without additional copper species.¹ Operating conditions have also been developed to incorporate both methacrylates and styrene using sequential monomer feeds, thus extending the range of well-controlled multiblock materials that can be efficiently synthesized.² The process provides a flexible and relatively low cost means to scale up the production of block copolymers using reactor systems and reaction times similar to those currently used to commercially produce coating resins and specialty polymers by conventional radical polymerization chemistry.

1. Shirali Zadeh N., Cooze M. J., Barr N. R., Hutchinson R. A., *React. Chem. Eng.* 4:2000-2010, 2019.
2. Cooze M. J., Deacon H. M., Phe K., Hutchinson R. A., *Macromol. React. Eng.* 16:2100043, 2022.

L-01

WALL SLIP AND INSTABILITIES IN CAPILLARY FLOW OF LUBRICATED POLYETHYLENE MELT

Z. Starý, M. Nevoralová, A. Rakitina

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Production of polymer products by extrusion such as tubes, films, fibres or profiles is governed to a large extent by flow behaviour of processed polymer melt. The main limitation of the production rate is the onset of flow instabilities manifested by melt fracture phenomena, such as sharkskin, stick-slip and gross melt fracture. These effects occur when the shear stress at the wall exceeds a critical value.¹ Another phenomenon so called melt rupture is related to the instability of the elongational flow when the melt enters the die. In order to postpone the onset of these effects to higher throughputs different types of processing aids or lubricants are used. In general, these compounds act at the wall-polymer interface, decrease the wall shear stress and promote wall slip.²

In this contribution the complex effect of stearate-based processing aid on wall slip and flow instabilities of polyethylene melt in both shear and elongational flow is investigated using high-pressure capillary rheometry.

1. Agassant, J.-F.; Arda, D.R.; Combeaud, C.; Merten, A.; Münstedt, H.; Mackley, M.R.; Robert, L.; Vergnes, B., *Intern. Polym. Proc.* 2006, 3, 239-255.
2. Kharchenko, S.B.; Migler, K.B.; Hatzikiriakos, S.G. *Conventional Polymer Processing Aids in Polymer Processing Instabilities*, Eds. Hatzikiriakos, S.G. and Migler, K.B, CRC Press 2020, Boca Raton.

Acknowledgement: *The authors thank the Technology Agency of the Czech Republic (project nr. TH04020353) for financial support.*

L-02

PREPARATION AND PROPERTIES OF COMPOSITES WITH HYBRID NANOFILLERS

Y. Soyka^a, M. Procházka^a, M. Mičušík^a, V. Špaček^b, K. Zetková^b, M. Omastová^a

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The combination of nanofillers and the epoxy matrix, which merges the advantages of epoxy resin and nanomaterials, is successful way to fabricate progressive composites. Mixing MXenes and CNTs in the epoxy matrix increases the conductive properties of the composites, which leads to various application as EMI shielding, conducting painting, etc.

MXenes are a large family of two dimensional (2D) materials with unique optoelectronic properties and tuneable surface termination. MXenes are made by etching of the “A” layers from MAX phase, where M is the most common transition metal, A is an element of the 13 or 14 group of the periodic table of elements, X is usually C and/or N.¹

Carbon nanotubes (CNTs) in polymeric matrices have a great influence on electrical conductivity, shear strength and other transport properties of prepared composites, due to its excellent mechanical and physical properties.²

Nanofillers as Ti₃C₂ type of MXenes (Drexel University) and CNTs Nanocyl 7000 (NANOCYL, Belgium) have been used for experiment. Also Bisphenol A, glycidyl epoxy called CHS-EPOXY® 582, and Telalit® 0420 hardener (Spolchemie, Czech Republic) were used for polymeric matrix for preparation. The composites with different concentration of nanofillers were prepared by solvent casting method. MXenes solution was mixed with epoxy resin using mechanical stirrer, while CNT were mixed with ethanol in ultrasonic bath first. Three types of composites were prepared, epoxy/MXenes, epoxy/CNT, and epoxy/MXenes and CNT. For hybrid composites CNT preparation, suspension of CNTs in ethanol were added to epoxy/MXenes dispersion and all compound were mixed together by magnetic stirrer. After that, the hardener was added and mixed for 15 min by hand and composites were poured into round shapes form. Composites were dried in the air overnight and then 4-6 h in vacuum oven at 60 °C. The conductivity of samples was measured by BDS method.

The hybrid composites were more conductive than epoxy/MXenes or epoxy/CNT. All composites provide good flexible properties. Using hybrids of nanoscale fillers and additives "smart" composite materials were obtained, with application as sensitive pressure switch or strain sensing.³

1. Naguib M., Kurtoglu M., Presser V. *et al.*, Adv. Mat. 23 (37): 4248-4253, 2011.
2. Dinesh Kumar S., Ravichandran M., Alagarsamy S.V. *et al.*, Mater. Today: Proceedings, 27:1152-1156, 2020.
3. Monastyreckis G., Stepura A., Soyka Y., Maltanova H., Poznyak S.K., Omastová M., Aniskevish A., Zeleniakiene D., Sensors 21:2378, 2021.

Acknowledgement: *This work has received funding from the European Union’s Horizon 2020, grant agreement No 777810, and from project VEGA 02/0006/22 (Slovakia).*

L-03

SUSTAINABLE THERMOPLASTIC MATERIAL BASED ON POTATO STARCH AND NATURAL RUBBER

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Sustainable modified thermoplastic potato starch (TPS) with broad mechanical properties, good hydrophobicity, and adequate biodegradability has been developed. It is an eco-friendly material made from potato starch, natural rubber (NR) and epoxidized natural rubber (ENR). The addition of NR and ENR solved the problems of poor mechanical properties and high-water absorption of thermoplastic potato starch. The mixture of polar TPS and non-polar NR prepared in an internal mixer shows poor compatibility. This is the main problem limiting the properties of the blends. Morphology, mechanical properties, water absorption and biodegradability of studied blends are evaluated. The results show that ENR can be used as a compatibilizer for NR and TPS blends. As the rubber content (mainly ENR content) increases, the tensile strength of the material decreases and the elongation at break increases. With the increase of ENR content (ENR > 30%), the change of various properties of the material is more significant. The development of ternary blend compositions enables the modified materials to possess the desired mechanical properties and lower price. Blends with low rubber content biodegraded after 1 week. The developed material can be processed by compression molding or extrusion. TPS, unvulcanized NR, ENR are all natural green materials, which provide new ideas for the development of environmentally friendly materials. Potential applications for this naturally derived TPS/NR/ENR material include agricultural films, packaging, and more. In future work, we will focus on developing different functional biomaterials based on starch/rubber composites to broaden the properties and applications of starch-based materials. ¹

1. Cai Z., Čadek D., Šmejkalová P. *et al.*, *Materials Today Communications*, 26, 101912, 2021.

Acknowledgement: *This work was co-supported from the grant of Specific university research – grant No.: A1_FCHT_2022_004 and A2_FCHT_2022_005 in the project application number from IGA and by the ESF in OP RDE – project No.: CZ.02.2.69/0.0/0.0/19_073/0016928.*

L-04

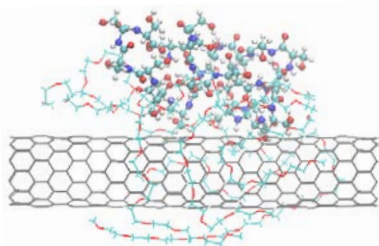
ADSORPTION OF MONOPEPTIDES ONTO CARBON NANOTUBES GRAFTED WITH POLY(ETHYLENE OXIDE) CHAINS. MOLECULAR DYNAMICS STUDY

Z. Benková^a, P. Čakánek^a, M. N. D. S. Cordeiro^b

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Carbon nanotubes (CNTs) have attracted a great deal of scientific attention due to their wide range of applications. The use of CNTs in biomedicine requires the modification of CNT sidewalls to increase their solubility in water and to protect CNT from undesired protein adsorption. This might be achieved by modification of CNTs with biocompatible polymer chains. The interactions between CNT irreversibly covered by poly(ethylene oxide) (PEO) chains at different grafting densities and mono-peptides built up of glycine, serine, or valine have been studied using molecular dynamics simulations. In order to assess the effect of hydration and physiological concentration of NaCl on the peptide adsorption, the simulations have been carried out in a vacuum, water, and saline. The presence of NaCl virtually does not affect the adsorption of the peptides, except for polyserine, which interacts with the PEO layer through the sodium cations acting as bridges. The investigated peptides are adsorbed on CNT in all environments regardless of the grafting density of the PEO chains. The peptides adhere to the PEO layer without its compression. In a vacuum, the binding free energy of the peptides, with the largest contributions due to the van der Waals interactions, exceeds the binding free energy in water and saline. The reduced number of van der Waals interactions between the peptides and the CNT sidewall induced by the presence of PEO chains is compensated by the formation of new van der Waals and Coulomb contacts between the peptides and PEO chains. In water and saline, the increase of entropy due to the expulsion of water molecules from the PEO layer, which is more significant at lower grafting density, is also supposed to support the peptide adsorption. In some systems, flexible polyglycine and partly polyserine adopt conformations elongated along the CNT axis upon adsorption to maximize the number of favorable interactions with the CNT sidewall. The adsorption of peptides is responsible for reduction of intramolecular hydrogen bonds in peptides and transformation of their secondary structures.



Snapshot of CNT grafted with PEO chains at grafting density 0.388 nm^{-2} interacting with polyserine in water. Water molecules are omitted for clarity. Polyserine is represented by the ball-and-stick model.

Acknowledgement: This work was supported by grants APVV-21-0346, VEGA 2/0122/20, and UID/QUI/50006/2020.

L-05

MODIFICATION OF CHITOSAN BY PERMANENTLY CHARGED CATIONIC AND ANIONIC MOIETIES: AN INTERESTING SCIENCE BEHIND AT GLANCE SIMPLE APPROACHES

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Chitosan is a linear polysaccharide predominantly composed of glucosamine (GlcN) unit which is classified as a weak cationic polyelectrolyte. GlcN contains an ionizable primary amino group with a pK_a value of 6.4. The solubility of chitosan in an aqueous environment is dictated by the level of protonated amino groups in the GlcN unit. Thus, chitosan is insoluble at the physiological pH of ~ 7.4 , which represents a major drawback for using chitosan in applications requiring solubility or polyelectrolyte complex formation at the physiological pH. The conjugation of cationic or anionic pendant moieties to chitosan has been considered as a straightforward approach for obtaining strong ionic chitosan-based polyelectrolytes soluble at neutral pH.

The subject of this study was introducing either quaternary ammonium¹ or sulfopropyl² groups to the chitosan backbone. The product of the reaction is charged chitosan containing positively or negatively charged moieties, respectively, and an equivalent amount of counterions. The chitosan derivatives with the degree of substitution (DS) between 20 and 100 % were synthesized in aqueous solutions. The DS of the charged chitosan derivatives was controlled by changing the feed molar ratio of glucosamine to the modifying agents. We established that the true DS of modified chitosan is determined by ¹H NMR. Surprisingly, the methods widely used in the literature to determine the DS values of both permanently charged cationic and anionic chitosan derivatives provide up to around 80 % lower DS values compared to those found by us using NMR. We identified that this observation can be ascribed to a presence of high content of unexpected counterions in the structure of charged chitosan derivatives originating from the aqueous solutions during the selected synthesis process and the applied purification conditions.

1. Heydari, A., Dušička, E., Mičušík, M. *et al.*, *Polymer*, 220:123562, 2021.
2. Heydari, A., Darroudi, M., Lacík, I. *Reaction Chemistry & Engineering*, 6:2146-2158, 2021.

Acknowledgement: *This work was supported by the Juvenile Diabetes Research Foundation (JDRF) Grant No. 2-SRA-2018-521-S-B, the Chicago Diabetes Project, the Slovak Research and Development Agency under the contract numbers APVV-18-0480 and APVV-20-0272, and the Slovak Grant Agency VEGA 2/0140/20. This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF.*

L-06

A NEW CHIRAL MEMBRANES FOR RACEMIX MIXTURE SEPARATION

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A series of membranes was prepared and successfully applied in both sorption and pertraction experiments. New nano-micro membranes underwent sorption tests, soaked in an aqueous solution of the model chiral drug D, L-Trp. The evolution of enantiomeric concentration over time was monitored by HPLC analysis and revealed no sorption activity for a blank membrane – i.e., one lacking a chiral selector. On the contrary, the membranes containing the selector demonstrated preferential sorption activity towards one enantiomer. The sorption of L-Trp was found to be proportional to the fraction of the chiral selector in the active layer of the membrane, while an unchanged concentration of D-Trp was detected in the solution during the entire testing time interval. In addition, an enantiomeric separation of the same model chiral drug was performed in by pertraction in diffusion cells. The preferential sorption of L-Trp from the feed underlined the crucial importance of the selector in the active layer to achieve chiral recognition of enantiomers. Due to the exclusive membrane material, the retention of L-Trp in the membrane materials did not block the transport of D-Trp into the permeate during the entire experimental time. Moreover, only 50% of DACH in one part of the active layer was sufficient to achieve an enantioselectivity of 99%. Fresh and used membranes were analyzed by FTIR spectroscopy and characterized by SEM. The role of the PA active layer in chiral recognition of Trp enantiomers was elucidated. This study demonstrates that such membranes can be an effective tool for the separation of enantiomers.¹

Acknowledgements: The authors gratefully acknowledge Czech Science Foundation grant 20-06264S for financial support.

1. J. Gaálová, F. Yalcinkaya, P. Cuřínová, M. Kohout, B. Yalcinkaya, M. Koštejn, J. Jirsák, I. Stibor, J. E. Bara, B. Van der Bruggen, P. Izák, Separation of racemic compound by nanofibrous composite membranes with chiral selector, *Journal of Membrane Science*, 596 (2020) 117728.

L-07

BIG SCIENCE WITH SMALL FOOTPRINT

S. Kukla

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L-08

CU(0)-RDRP OF 2-HYDROXYETHYL METHACRYLATE IN A NON-POLAR SOLVENT: RAPID SYNTHESIS OF WELL-DEFINED, HIGH-MOLECULAR WEIGHT (CO)POLYMERS

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Poly(2-hydroxyethyl methacrylate) (poly(HEMA)) is an important functional polymer with favourable properties, such as biocompatibility and non-toxicity, and numerous applications particularly in the biomedical field.¹ Unsurprisingly, ever since the inception of the copper-mediated reversible deactivation radical polymerization (Cu-RDRP), HEMA polymerization has been pursued by many authors who employed various Cu-RDRP protocols in polar solvents. Intriguingly, these methods universally failed at producing well-defined poly(HEMA) of molecular weight (MW) higher than approximately 50 000 and, due to the solvent polarity, were not particularly suitable for the synthesis of HEMA-based amphiphilic copolymers unless a cumbersome protection/deprotection strategy was employed. In this study, we investigated the applicability of copper wire-mediated Cu(0)-RDRP, conducted in 1,4-dioxane as a comparatively non-polar solvent, to HEMA (co)polymerization. Rapid and well-controlled (co)polymerization of HEMA, was achieved via Cu(0)-RDRP using ethyl α -chlorophenylacetate as an initiator and PMDETA as a ligand. The addition of a small amount of CuCl₂ as a deactivator afforded very well-defined ($D \leq 1.26$) HEMA homopolymers in an unprecedentedly wide range of molecular weights from 10 000 to approximately 500 000. On the other hand, the structurally analogous bromine-based initiation/catalytic system led to an uncontrolled polymerization. To exemplify the utility of using a non-polar medium for HEMA polymerization, we conducted a copolymerization of HEMA with an equimolar amount of a lipophilic comonomer, lauryl methacrylate (LMA), yielding a well-defined ($D = 1.09$) amphiphilic poly(HEMA-co-LMA) copolymer with quantitative conversion.

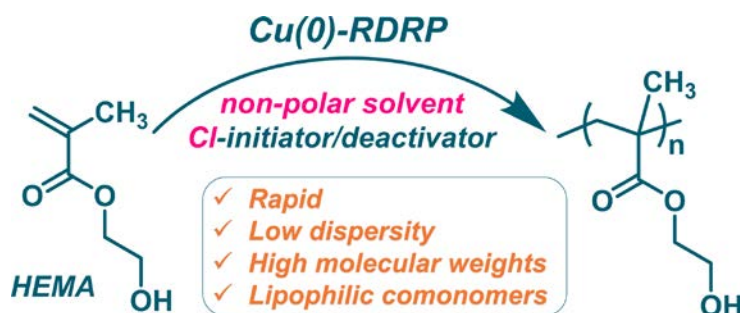


Figure: Cu(0)-RDRP of HEMA in 1,4-dioxane with chlorine-based initiation/catalytic system affording well-defined (co)polymers

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Acknowledgement: SG thanks the Institute of Macromolecular Chemistry, CAS, for supporting his participation at this conference.

L-09

ADDUCTS OF TRICHLOROACETYL ISOCYANATE: A NEW CLASS OF MULTIFUNCTIONAL INITIATORS FOR COPPER-MEDIATED RDRP

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Trichloroacetyl isocyanate (TAI) is known to react extremely rapidly and cleanly with a range of functionalities, including hydroxy and amino groups, which is extensively used for analytical purposes. In this study, we reveal that TAI adducts act as efficient multifunctional initiators of copper-mediated reversible-deactivation radical polymerization (Cu-RDRP). A great variety of substrates can thus be transformed into Cu-RDRP (macro)initiators with unprecedented ease.

Using the TAI/methanol adduct (Figure 1) as a model initiator, we identified conditions for well-controlled Cu(0)- and/or Cu(I)-catalyzed Cu-RDRP of model monomers [styrene, methyl acrylate, and methyl methacrylate (MMA)], performed both in polar and non-polar solvents, affording defined polymers in a wide range of molecular weights. The developed conditions were then successfully applied to other acrylates and methacrylates, including polar ones. Importantly, via NMR and viscometric analyses, we established that the TAI-borne (trichloroacetyl) group can initiate up to three polymeric chains for all the studied monomer classes, which may be of a great importance in applications such as surface-initiated grafting. Furthermore, using the “bifunctional” ethylene glycol/TAI adduct, model poly(2-hydroxyethyl acrylate) was prepared and used for confirming the hydrolytic stability of the carbamate group within the initiator fragment in the pH range of 5 to 9.

Finally, we demonstrated the utility of the TAI-modification strategy in the chain topology control by performing a (de novo) one-pot synthesis of a graft copolymer, exploiting the in situ modification of a pre-formed poly(HEMA-co-MMA) copolymer with TAI. Additionally, we also exemplified the applicability of the TAI adduct-initiated Cu-RDRP in the modification of natural materials. For instance, unprecedented instantaneous modification and dissolution of cellulose in DMSO upon the addition of a slight stoichiometric excess of TAI was achieved, and the prepared cellulose-TAI adduct was then successfully used for MMA grafting, affording bottle-brush type copolymers. Similarly, the surface of filter paper was modified with TAI with spatial control, allowing for the growth of a macroscopic polymeric brush pattern in a subsequent step. In summary, the multifunctional TAI-based initiators hold a great promise for the facile preparation of complex polymeric architectures.

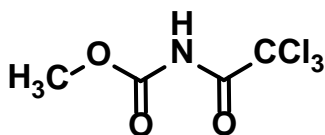


Figure 1. The structure of the methanol-TAI adduct.

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L-10

ANTIFOULING SURFACES VIA INTERFACE-MEDIATED PHOTOINDUCED ELECTRON/ENERGY TRANSFER REVERSIBLE ADDITION–FRAGMENTATION CHAIN TRANSFER (PET-RAFT) POLYMERIZATION

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Nonspecific adsorption of biomolecules at solid interface can impair the performance of materials that are brought into contact with biological media. In particular, nonspecific adsorption of proteins (fouling) can ultimately lead to malfunction of many biotechnological and biomedical devices. Some examples include bacterial attachment to contact lenses, nonspecific response of affinity biosensors, reduction of circulation time of nanocarriers in blood stream or disabling of cardiovascular devices by thrombus formation.

It has been shown, that protein fouling can be reduced or even completely prevented by surface modifications with polymer brushes.¹ Polymer brushes can be prepared by one of several available reversible deactivation radical polymerization (RDPR) techniques. Among various RDPR methods, interface-mediated reversible addition-fragmentation chain transfer (RAFT) polymerization has emerged as a powerful tool for their synthesis. Utility of RAFT process arises from its relatively high tolerance to residual oxygen presence, wide variety of polymerizable vinyl monomers, experimental simplicity, and no need for metal catalysts. However, the conventional RAFT process requires elevated temperatures to provide a continuous source of radicals, and thus cannot be directly used in the presence of temperature sensitive biological entities.

To address this limitation, photoinduced electron/energy transfer RAFT polymerization (PET-RAFT) has been proposed as a promising alternative to the thermally induced systems. More recently, PET-RAFT technique has been successfully utilized for the preparation of antifouling polymer brushes using light-emitting diodes (LEDs) with a maximum intensity at 410 nm.²

Herein, we present a simple and universal methodology enabling the synthesis of antifouling poly(*N*-(2-hydroxypropyl)methacrylamide) (poly(HPMA)) brushes in a well-controlled manner via interface-mediated PET-RAFT technique using yellow light with the maximum intensity at 560 nm. To achieve this, we developed an aqueous system based on water-soluble RAFT agent, zinc-tetraphenylporphyrin (ZnTPP) acting as photosensitizer, and LEDs-based photoreactor as the light source.

Acknowledgements: *The authors gratefully acknowledge the Grant Agency of the Czech Republic (Grant nr. 20-15077Y and 20-13946Y) for the financial support of this research.*

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L-11

POLYMER BLENDS COMPATIBILIZATION USING COPOLYMERS: MODIFICATION OF SIMPLE ESTIMATION METHODS

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Properties of polymer blends can be improved by compatibilization, modification decreasing interfacial tension and thus increasing adhesion between phases. It can be reached through addition of block or graft copolymers with blocks identical or miscible with or that adhere to related component of a polymer blend. There exist exact and sophisticated theories; however, relatively simple models providing formulae usable for material engineers without necessity of extensive computations are useful for applications. Such models allowing estimation of decrease in interfacial tension as a function of copolymer addition were published by Leibler¹, Noolandi², Retsos³.

Since there is an intermediate result, effective thickness of the interfacial layer, having no explicit analytical solution, simplified models for system parameters where the thickness can be expressed by approximate analytical formula were used in past years. These special cases were low copolymer content at the interface when copolymer molecules form Gaussian coils, and dry brush approximation for copolymer in high concentration with a chain shorter than homopolymers, and wet-brush approximation for copolymer with a chain longer than homopolymers. The problem was in discontinuity between the dry brush regime results and results of other method. Systems with intermediate copolymer concentrations at the interface were adequately described by none of the simplified models.

In our recent paper⁴, we decided to change the calculation so that the input parameter is the resulting copolymer content in the interfacial layer, while the corresponding total copolymer content in the system (which is physically the independent system parameter) is the calculation result together with a decrease in the interfacial tension. This allowed us to use full expression for interfacial layer thickness without approximation. When the validity conditions of the dry- or wet-brush approximation were met, the results obtained using the new procedure were consistent with those obtained using the appropriate approximation. Interfacial copolymer contents and decreases in interfacial tension obtained for systems where neither the dry-brush nor the wet-brush approximation were applicable lied between results of both mentioned approximations.

Consequently, we are trying to refine various previous results using new procedure avoiding the dry- and wet-brush approximations.

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L-12

INFLUENCE OF WASTE RUBBER POWDER (WRP) ACTIVATION TEMPERATURE ON THE BEHAVIOR OF WRP-MODIFIED RUBBER MATRIX

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The increasing amount of rubber waste, namely tires, represents economic, social and ecological problem. The inclusion of these materials in the circular economy and the search for their applications is one of the current challenges. End of Life tires looks as a valuable resource that could save part of raw materials for new production. To use the full potential of rubber waste, it is necessary to partially “devulcanize“ or “activate“ the surface of waste rubber powder (WRP).

The aim of this study was to describe the effect of the activation temperature on the final properties of the WRP-modified rubber matrix. The WRP (particle size < 0.4 mm) was activated thermo-mechanically in lab banbury at different temperatures (80, 100, 120, 140 and 160 °C). For each activation temperature, we prepared two rubber compounds having WRP concentrations 7 and 14 %, well as the compound with non-activated WRP and no WRP standard. The compounds were characterized by relevant testing methods (Mooney viscosity, course of vulcanization, tensile test, hardness test, DMA, SEM, etc.).

L-13

IONIC LIQUID-INDUCED FORMATION OF BIO-SOURCED EPOXY NETWORK

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In this work we have developed a simple VOC-free tricomponent reaction platform for the stoichiometric polymerization between diepoxy resin and dicarboxylic acid mediated by an imidazolium-based ionic liquid under mild conditions (80 °C, atmospheric pressure). Due to the abundance of bio-sourced epoxy resins and dicarboxylic acid compounds and the vast number of their combination allowed by this platform, we believe it could be adaptable for manufacturing products of the fast-growing bio-based epoxy resin market. We demonstrate in detail the mechanism of epoxy copolymerization with the dicarboxylic acid and define limiting parameters of the reaction to take place in a way, that avoids the competition with the epoxy homopolymerization (up to now the most well-studied ionic liquid-epoxy reaction). Consequently, this platform will be useful for polymer chemists to expand their options of binding bio-building blocks for complex epoxy networks.¹

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SPECIAL POLYOLEFINS BY CHAIN WALKING CATALYSTS

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Polyolefins are typically used in low-added-value applications such as packaging, pipes or simple constructions. Use of chain-walking catalysts can provide very special polyolefins with linear to dendritic topology and can introduce functional groups.^{1,2} Such polyolefins are not accessible by any other polymerization technique and may find completely new applications where combination of highly hydrophobic polyolefin with polar functionalities is essential. Here, we present our recent advances in strategies to incorporate functional groups into branched polyolefins and their use for preparing of amphiphilic block and grafted copolymers combining living coordination chain-walking mechanisms with ROP or ATRP.

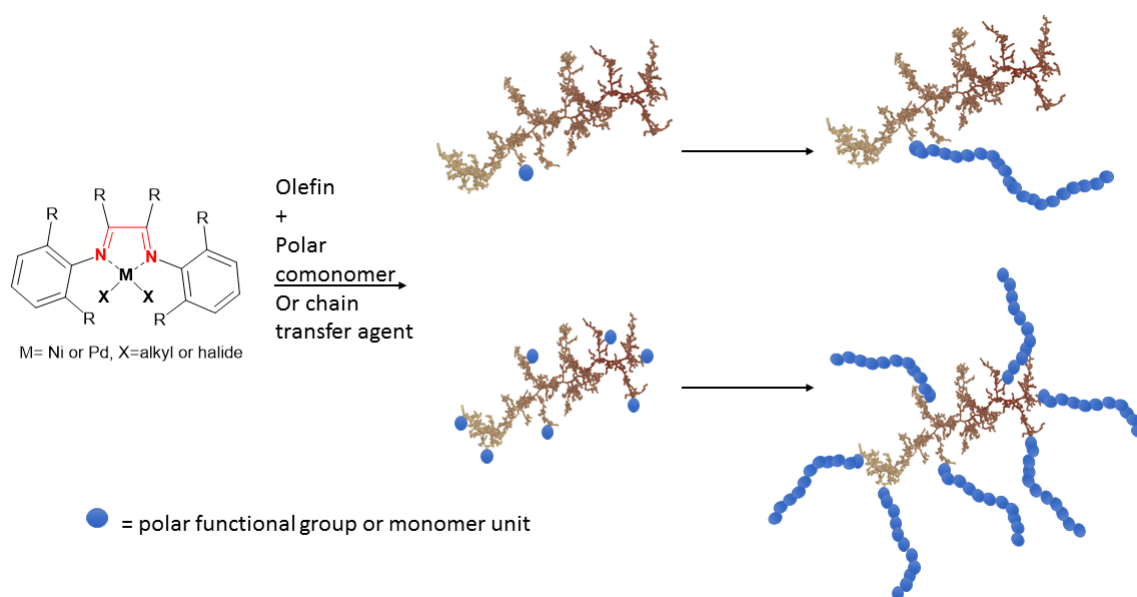


Fig. 1 Amphiphilic copolymers with dendritic polyolefin blocks

Acknowledgement: This work was supported by the Czech Science Foundation (No. 22-09470L) and from specific university research (MSMT No 20-SVV/2022).

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L-15

POROUS HYPER-CROSS-LINKED POLYMERS PREPARED VIA TEMPLATING METHOD

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A series of hyper-cross-linked polymers (HCPs) with polyacetylene main chains and Schiff base segments have been prepared through coordination chain-growth homo- and copolymerization approach.^{1,2} Aromatic Schiff base-type (bearing –CH=N– groups) monomers substituted with one or more polymerizable ethynyl groups have been used as a source of template-bearing segments and 4,4'-diethynylbiphenyl or tetrakis(4-ethynylphenyl)methane have been used as cross-linkers for copolymerization approach. The copolymerization has been initiated with [Rh(nbd)acac] complex and provided HCPs. Porosity of HCPs has been controlled by covalent structure.

The –CH=N– groups of the parent HCPs were found to be smoothly and quantitatively dissociated by acid hydrolysis, resulting in HCPs with modified texture. Detemplating of HCPs led to the generation of porosity of originally non-porous polymers or to modification of porosity of originally porous polymers. Simultaneously, reactive groups like –CHO or –NH₂ were introduced to the polymers. The template-free HCPs decorated with these groups acted as a chemisorbents for covalent trapping of low molecular weight aldehydes or primary amines. Moreover, prepared porous HCPs were effective for physisorption of gaseous adsorptives (N₂, CO₂, I₂).

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Acknowledgement: *Financial support from the Czech Science Foundation (Project 21-02183S and 20-01233S) is gratefully acknowledged.*

L-16

CHAIN WALKING POLYETHYLENE AS IMPACT STRENGTH MODIFIER OF POLYSTYRENE

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Ethylene-based elastomers can be prepared by ethene homopolymerization using chain walking catalysts.¹ Such materials are composed of highly branched polyethylene molecules (cwPE) with low crystallinity and low T_g . These properties cause the material to have an elastomeric character. This project aims to use cwPE prepared with Ni diimine catalysts as an impact strength modifier for polystyrene by generating a two-phase structure material analogous to the commercially produced high impact polystyrene (HIPS) where dispersed phase of polybutadiene rubber absorbs the kinetic energy of impacts and stops the spreading of cracks. Our intention is to substitute the commonly used polydiene phase susceptible to oxidation by saturated hydrocarbon cwPE rubber readily accessible by ethene only homopolymerization. Improvement of compatibility of the two immiscible phases in HIPS is achieved by *in-situ* formation of grafted copolymer polybutadiene-*g*-PS during HIPS manufacture by radical polymerization of styrene solution of polybutadiene. This is the strategy, which we want to adopt here: using cwPE with high amount of branching points that can be attacked by radical initiator used for styrene polymerization and therefore can serve as initiating centers for growth of PS grafts to form cwPE-*g*-PS graft copolymer acting as a compatibilizer. To further facilitate the formation of cwPE-*g*-PS, the copolymerization of ethene with non-conjugated dienes² to yield cwPE functionalized with double bonds was investigated too.

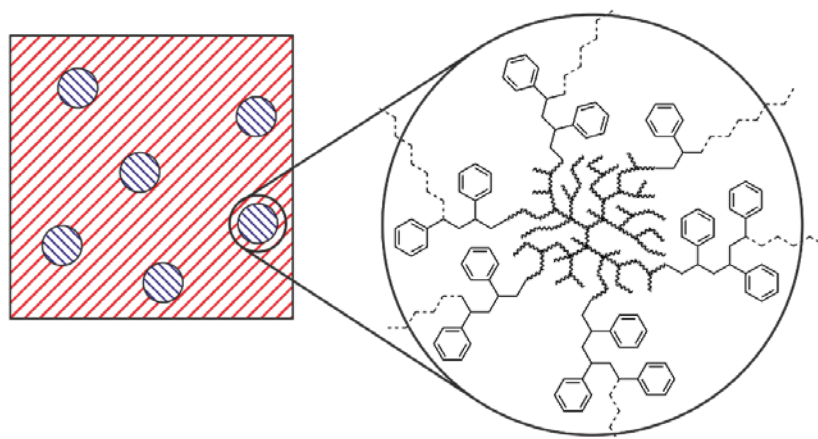


Figure 1: Scheme of material based on polystyrene matrix (red) with dispersed cwPE elastomer particles (blue)

Acknowledgement: This work was supported by the Czech Science Foundation (No. 22-09470L) and from specific university research (MSMT No 20-SVV/2022).

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L-17

POROUS IONIC HYPER-CROSS-LINKED POLYACETYLENES WITH CHIRAL AND ACHIRAL SEGMENTS

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Several methods have been developed for the preparation of porous hyper-cross-linked polyacetylene networks containing ionic pyridinium units either as pendant group or cross-links. The methods combined (i) chain-growth polymerization in which the ethynyl groups of the monomers were transformed into unsaturated polyene main chains of the networks and (ii) quaternization reactions transforming pyridine segments into segments of *N*-alkyl pyridinium type. Networks with micro/mesoporous texture (S_{BET} up to 590 m²/g) and a high and tuneable content of pyridinium units (up to 7.9 mmol/g) were achieved. The micro/mesoporosity reflected the rigidity of the unsaturated main chains and aromatic cross-links of the networks. The used quaternization techniques made it possible to introduce ionic groups with various compositions, including chiral groups, into the networks. The networks were efficient in reversible capture of water from the air and as heterogeneous catalysts for the conversion of styrene oxide and CO₂ to styrene carbonate.

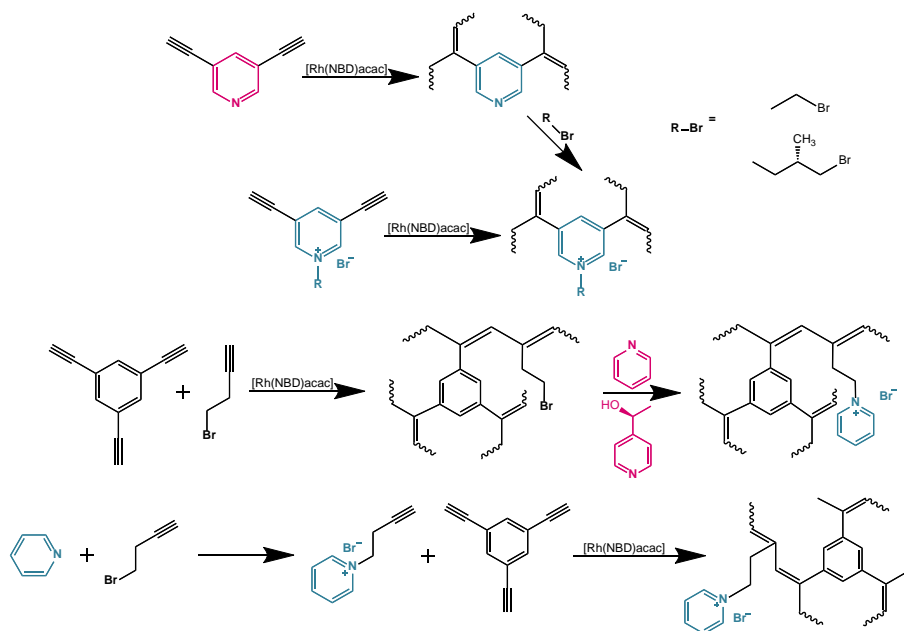


Figure 1. Preparation of ionic porous polyacetylene networks with pyridinium segments.

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L-18

SUSTAINABLE POLYITACONIC ACID / NANOCCLAY HYDROGELS

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Due to rising environmental concerns, interest about renewable materials has grown significantly in recent years in all industrial fields, particularly in polymer industry. While the majority of polymers is currently produced from petrochemical feedstock, a huge shift towards renewable (bio-based) monomers and more sustainable polymers is expected in near future. Itaconic acid is renewable unsaturated dicarboxylic acid rated as one of the twelve most important biomass-derived compounds that can be transformed into a wide range of valuable chemicals or materials.

Herein, we investigate sustainable polyitaconic acid (PIA) / nanoclay hydrogels, which are prepared by fast and environmental-friendly supramolecular assembling.¹ Moreover, a renewable PIA is synthesized using mild daylight-induced initiator-free polymerization at ambient temperature.² In this contribution, the key roles of ionic interactions and nanoclay dispersants on the formation, structure and properties of PIA / nanoclay hydrogels are highlighted. The prepared hydrogels can find a wide range of potential applications as self-healing materials, fast stimuli-response sensors, sorbents of toxic compounds, superabsorbents, drug-delivery systems, 3D-printable composition, artificial muscles, etc.

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L-19

POLYUREA PROTECTIVE COATINGS WITH FAST DRYING TIMES. UNDERSTANDING OF CROSSLINKING FILM FORMATION.

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Polyurea coatings nowadays represent a very attractive material choice in the multiple coating applications including protective coatings for heavy environmental conditions. They draw much attention because of reduced solvent and catalyst demands in their technology and they even provide the possibility to formulate solvent-free systems. They possess high chemical resistance, high hardness while retaining flexibility, durability, abrasion resistance, and adjustable cure rate. Polyurea can be prepared from addition reaction of functional amines and isocyanates. At first part, we investigated the synthesis of N-substituted amine components from various primary amines and dialkyl maleate esters by the aza-Michael addition, so called “aspartate esters of aspartates”. We synthesized aspartates of different functionalities while the yield reached always at least 80%. Then, we studied the cross-linking reaction of the aspartates including an external cycloaliphatic reference aspartate “Desmophen NH 1420” of Covestro with tri-functional isocyanate Desmodur eco N 7300 (biobased type, Covestro). We observed a significant difference of the gel time determined for the same crosslinking composition including catalyst and solvent when reacting in bulk (closed vials) vs. when applied as open films that were drying under normal laboratory environment. We note that visual drying of these materials at RT was very fast (10¹ minutes). In closed systems, the gel time was longer, compared with the open systems while the differences ranged from several minutes to hours. This pronounced difference of gelation could not be explained only by the effect of external humidity – which could cause conversion of some isocyanate to primary amine that would further participate in crosslinking. We hypothesize, that the aspartate-based systems provide excessive intermolecular interactions based on H-bonds, causing rapid physical drying of the open films. This property provides advantage when handling coated objects in application and should be further investigated. In our contribution we discuss the unique effects of accelerated gelation in the open films and put forward physical explanation.

HYDROGELS MAY TURN STIMULI-RESPONSIVE UNDER STRAIN

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The stimuli-responsive (or stimuli-sensitive or smart) gels represent a class of promising materials where a reversible change of volume or appearance (clear-opaque-white) is triggered by an external stimulus (temperature, pH, ions, etc.). The applications include various gel actuators, drug delivery, tissue engineering, smart optics, temperature sensors, valves, etc. The phenomenon of such volume phase transition in polymer gels was predicted first¹ and after ten years experimentally confirmed² with partly hydrolyzed poly(acryl amide). Since then, the research on smart gels has grown to the specialized field of macromolecular hydrogel chemistry.

Recently, we have predicted³ based on a swelling model that VPT in hydrogels may be triggered by external strain. Our model is based change of Gibbs energy composed of two contributions, the swelling term derived from the classical Flory-Huggins theory and the elastic term based on Kovac's model of elasticity³ considering the final extensibility of chains. Some synthetic hydrogels for which the response to a stimulus such as temperature has not been observed so far, e.g., lightly crosslinked poly(2-hydroxyethyl methacrylate), under strain may reveal response to stimuli. Our incipient experimental data support this prediction. Such behavior will have an impact on the application of hydrogel constructs composed of two differently swelling hydrogel phases, such as core-shell particles, bi-layers, or in 3D-printed hydrogel specimen, where the swelling pressure of one phase may trigger the VPT in the other phase. Such effects may lead to shape distortion or loss of transparency but on the other hand, may open doors to advance hydrogel devices. In our contribution, the model will be explained as well as the impact of individual physical parameters on the VPT initiation, experimental progress will be reflected and several practical-related examples will be given.

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L-21

MOLECULAR STRUCTURE OF RECYCLED POLYMERS BY SIZE EXCLUSION CHROMATOGRAPHY AND ADVANCED DETECTORS

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The molar mass distribution and chain topology of various recycled polymers not only affect their properties, but also provide information about the possible degradation during the polymer use and/or recycling process. Size exclusion chromatography (SEC) is nowadays the dominant technique for the determination of molar mass distribution. SEC coupled with a multi-angle light scattering (MALS) detector and an online viscometer yields not only true molar mass, but also the information about the degree of branching.^{1,2} The contribution offers a brief overview of the fundamental principles of MALS and online viscometry and presents several examples of the application of the technique for the characterization of recycled poly(ethylene terephthalate), polyamides and poly(vinyl chloride). Examples of obtainable results are shown in Figure 1.

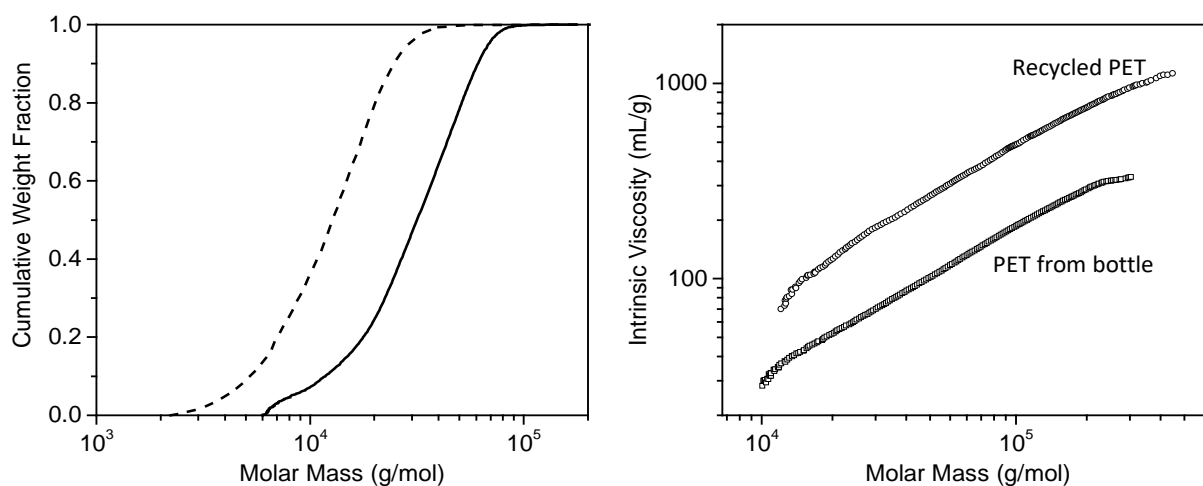


Figure 1 Cumulative molar mass distribution plots (left) of recycled polyester before (solid) and after (dashed) extraction from the fabric show significant degradation of polymer chains during extraction. The mutual shift of Mark-Houwink plots (right) of recycled PET and PET from a bottle of soft drink suggests different chain topology of the two polymers.

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NEW GRADIENT COPOLYMERS BASED ON ALIPHATIC AND AROMATIC 2-OXAZOLINES FOR PHOTODYNAMIC THERAPY

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Conventional cancer therapies, i.e. surgery, chemotherapy, and radiotherapy, have many side effects. Therefore, modern strategies based on targeted cancer therapy allowing selective tumor destruction are of increasing interest. Photodynamic therapy (PDT) is a unique treatment method that can cure superficial tumors, and as an adjuvant therapy, it can be used in conjunction with conventional treatment methods.¹ In PDT, light of a specific wavelength corresponding to the absorption band of a photosensitive drug activates the photosensitizer in the tumor. Broader utilization of PDT is limited by low water solubility, low chemical stability, and not efficient biodistribution of organic photosensitizers *in vitro* and *in vivo*. Here, we focused on encapsulation of hypericin as efficient naturally occurred photosensitizer by novel types of gradient copolymers based on aliphatic and aromatic 2-oxazolines. Gradient copolymers have been prepared via one-pot copolymerization of 2-ethyl-2-oxazolines with various 2-(4-alkyloxyphenyl)-2-oxazolines.² Prepared copolymers provided stable nanoparticle formulations with loaded hypericin with hydrodynamic diameter in the range of 50-200 nm. We demonstrated high loading capacity of nanoparticles and high photodynamic activity of loaded hypericin.

Gradient copolymers based on aliphatic and aromatic 2-oxazolines were used for encapsulation and delivery of quercetin, which belongs to class of dietary flavonoids and possesses a wide range of pharmacological activities, including neuroprotective, antioxidant, anticancer, antimicrobial, and antiapoptotic applications.³ Quercetin loaded nanoparticles were formed in self-assembly process. Size and colloidal stability of nanoparticles depended on composition of copolymers, amount of quercetin and method used for nanoparticles formation.

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POST-MODIFICATION OF MULTICOMPONENT PMCG MICROCAPSULES WITH POLYELECTROLYTES: IMPACT ON MICROCAPSULE CHARACTERISTICS AND BIOCOMPATIBILITY

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Transplantation of pancreatic islets immunoprotected by their encapsulation into polyelectrolyte complexation-stabilized alginate-based microcapsules is one of the strategies under development for normalizing the blood glucose level in type 1 diabetes patients.¹ The interpolyelectrolyte complex formed between anionic alginate and a cationic polyelectrolyte is deemed as beneficial for microcapsule stability and islet immunoprotection. This approach has been tested in clinical trials using human² as well as pig islets.³ However, the long-term graft islet function and survival were limited, with the pericapsular fibrotic overgrowth (PFO), induced by the foreign body reaction, being one of the key negative factors.⁴ It was postulated that the residual positive charge of polycations may be responsible for PFO.⁴ Therefore, understanding the correlation between the physico-chemical properties and biocompatibility of alginate-polycation microcapsules is needed. In this work, we used a specific type of multicomponent alginate-based microcapsule, the so-called PMCG microcapsule,⁵ as a model microsphere that was post-modified by various polyelectrolytes through dip-coating. The studied polyelectrolytes included chitosan-based polycations and polyampholyte, dextran-based polycation, cellulose-based polyanion, and cationic poly(2-methyl-2-oxazoline). The effect of post-modification was evaluated in terms of microcapsule physico-chemical properties (size, stability, morphology, permeability, residual surface charge), *in vitro* cell viability and cell adhesion, and microcapsule biocompatibility (presence of PFO *in vivo*, C57BL/6 mice model). This study shows that post-modification by polyelectrolytes is a viable strategy for modulating the physico-chemical characteristics and biocompatibility of interpolyelectrolyte complex-based microcapsules.

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L-24

THERMO-, pH- AND REACTIVE OXYGEN SPECIES-RESPONSIVE POLYMER CONTRAST AGENTS FOR ¹⁹F MAGNETIC RESONANCE IMAGING

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The dawn of fluorinated contrast agents in magnetic resonance imaging (MRI) greatly improved image quality due to the high sensitivity of ¹⁹F MRI negligible amount of endogenous fluorine atoms in the body. We have recently developed a conceptually new stimuli-responsive fluorine-containing polymer platform tailored for the use as contrast agents in ¹⁹F MRI. The applicability was demonstrated both in vitro and in vivo on animal models. The doubly pH- and thermo- responsive *N*-(2,2-difluoroethyl)acrylamide (DFEA)-based polymers were used to prepare ¹⁹F MRI – visible injectable depots with tunable dissolution rate.¹ The block copolymers hydrophilic biocompatible block – thermoresponsive polyDFEA form core-corona nanogel particles from molecular aqueous solution upon heating from room to body temperature. These nanoparticles are clearly visible in ¹⁹F MRI. Should a ferrocene moieties be introduced into such copolymers, these copolymers exhibit responsivity to reactive oxygen species – ROS (Figure 1).² Hydrophobic ferrocene is oxidized in the presence of ROS to cationic hydrophilic ferrocenium leading to ROS-triggered nanoparticle disassembly and drug release from such theranostic system. With slight change in fluorinated moiety structure, the oxidation is also visible on ¹⁹F MRI making the whole system also ROS-sensing.³

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L-25

NOVEL BIOCOMPATIBLE POLYMER PROBES FOR DUAL ³¹P AND ¹⁹F MAGNETIC RESONANCE IMAGING

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Magnetic resonance imaging (MRI) of X-nuclei (³¹P and/or ¹⁹F) is a modern method for visualization tissue or physiological processes *in vivo*.¹ Despite their potential, ³¹P and ¹⁹F MRI are not widely used in clinical practice, mainly due to the unavailability of suitable exogenous probes. Such probes should consist of biocompatible and long-circulating material that provides favorable MR properties including suitable relaxation times and a high-intensity signal distinguishable from the biological background. To achieve these goals, we have developed novel water-soluble polymer zwitterions with a high content of phosphorus and/or fluorine atoms in their structures. For ³¹P MRI, we prepared a polymer probe based on *O*-(2-(methacryloyloxy)ethyl)*O*-(2-(trimethylammonium)ethyl)phosphorothioate (TMPC), which is characterized by the presence of a biologically rare phosphorothioate group that provides a signal shifted by 56 ppm compared to naturally occurring phosphate-containing molecules.² Statistical copolymers of TMPC with methacrylamide-based monomers bearing either 3,5-bis(trifluoromethyl)benzyl or 5-fluorouracil moieties were used as dual probes allowing visualization by both ¹⁹F and ³¹P MRI. As another dual probe, we also synthesized a homopolymer based on *O*-(2-(dimethyl(3-((2-methylacryloyl)amino)propyl)azanium)ethyl)*O*-(2,2,2-trifluoroethyl)phosphorothioate, combining fluorine and phosphorus atoms in one monomer unit. In addition to high and well-distinguishable MR signals, all prepared probes also provided suitable *T*₁ and *T*₂ relaxation times, which is a good prerequisite for their prospective clinical applications.

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MODIFICATION OF ACID-BASE EQUILIBRIA OF WEAK POLYELECTROLYTES IN COMPLEX FLUIDS

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Weak polyelectrolytes (WPE) are polymeric molecules comprising covalently linked monomers of a weak acid (or base). Unlike monomeric acids in WPE acid-base balance is not only determined by the bath pH, ionic strength and the dielectric constant of the solvent but also by the polymer's ability to regulate the charge (charge regulation, CR) and modify the local environment due to the complex interplay between the conformational degrees of freedom, solution entropy, electrostatic and excluded-volume interactions.

Practical applications of WPE rely on their utilization in multi-component complex fluid environments, in mixtures of molecular aggregates such as micelles, liposomes and nanoparticles where multiple (often weak) intermolecular interactions are active. In these complex fluids it is often observed that the responsiveness of the WPE to the environmental pH deviates from that predicted from the pKa value measured in single-component solutions of the WPE.

In the presented study we describe significant shifts of the titration curves and the measured pKa (up to about 1 pH unit) of a model WPE, polyacrylic acid (PAA) in solutions of PEO-based micelles of different size (and volume fraction). Titration experiments (potentiometric and FTIR-ATR measurements) in dilute, salt-free solutions of PAA (of a few molecular weights) indicate that micelles of Pluronics block-copolymers and Brij-S20 (Polyethylene glycol octadecyl ether) modify the acid-base equilibria of PAA, with only a minor effect on the acid-base behavior of monomeric acids (propionic acid). TEM and SAXS characterization reveal correlation between the pKa shift and the spatial re-organization of the PEO-based micelles in the presence of PAA at low pH.

The results suggest that coupling between weak hydrogen bonding of protonated PAA to PEO and steric interactions with non-charged micelles modify the charge-regulation of high molecular weight PAA probably due the conformational degrees of freedom of the PAA chains. The study highlights the origins of modified pH responsiveness of WPE in complex fluids.

Keywords: Weak polyelectrolytes, steric effect, self-regulation

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INTERACTIONS OF PROTEINS WITH SYNTHETIC POLYMERS

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Water-soluble polymers are prospective carriers for the construction of polymeric drug delivery systems. However, their hydrophobic or charged fragments make them prone to non-specific interactions *in vivo* which define their biodistribution. The isothermal titration calorimetry (ITC) allows the elucidation of the relevant interactions of synthetic polymers for biomedical applications with molecules in physiological fluids and to find structure-interaction relationships in synergy with other analytical methods.

This was demonstrated on several cases: 1) Polyelectrolytes in biological fluids form complexes with charged proteins and peptides. The formation of the interpolyelectrolyte complex is observed by ITC as a two-step process - Coulomb attraction of charged molecules accompanied by the endothermic heat signature and the precipitation of the complex itself, often with the contribution of exothermic hydrophobic interactions. 2) In a more complex case the polyelectrolyte is a part of amphiphilic block copolymer poly(styrene-*b*-(meth)acrylic acid) and exists in an aqueous solution in the form of micelles, bearing charged polyelectrolyte corona of varied sizes. Melittin, the main bioactive peptide from honey bee venom, was adsorbed on such micelles at different pH. The adsorption was always endothermic with the stoichiometry given by the degree of ionization of the polyelectrolyte. Melittin exists in the solution as a tetramer and is adsorbed in the first step “as is”, but for the longer polyelectrolyte chains, further dissociation of the tetramer was observed. The stoichiometry of the melittin binding for micelles was always lower than for the polyelectrolyte in the solution due to steric hindrances. 3) Non-charged thermoresponsive polyacrylamides were titrated with the bovine serum at varied temperatures to reveal two binding mechanisms - exothermic hydrophobic and endothermic polar. The nature of amide substituent had a decisive impact on the interaction mechanism in comparison with temperature and molecular weight. 4) Amphiphilic block copolymers poly (nonyloxazoline-*b*-ethyloxazoline), intended for the delivery of the GPCII inhibitor to the cell membrane, demonstrated tunable hydrophobic interactions with blood proteins depending on the block length. 5) The thermoresponsive brushes of poly(DEGMA-stat-4-vinyl pyridine), grafted to the surface of silica were adsorbing the proteins from blood plasma proportionally to the surface hydrophobicity, switchable with temperature.

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L-28

MODERN METHODS OF THERMAL AND MECHANICAL ANALYSIS OF POLYMERS

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L-29

WATER RESISTANCE OF LATEX COATINGS: EFFECT OF CROSSLINKING, FLUORINATED COMONOMER, AND POLYMERIZABLE SURFACTANT

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Common latex coatings suffer from poor water resistance, which often limits their practical application. We report on the preparation of polyacrylate latexes using various approaches to tune the water resistance, wettability, and surface properties of their coating films. The mutual effects intra- or interparticle covalent crosslinking (introduced by allyl methacrylate copolymerization and keto-hydrazide reaction, respectively), fluorinated monomer copolymerization, and surfactant type (polymerizable and general) were investigated. The latexes were prepared by a two-step semi-continuous emulsion polymerization of 2,2,2-trifluoroethyl methacrylate, methyl methacrylate, butyl acrylate, and methacrylic acid as the basic monomers, where the fluorinated monomer was copolymerized into the second-step polymer (in the content of 30 wt. % based on the second-step monomer feeds). Water resistance, wettability, and surface properties of coating films were evaluated with a focus on water absorption, water whitening, water contact angle, and surface topography using atomic force microscopy. It was found that highly water-resistant and hydrophobic latex coatings that possess the self-healing ability were prepared provided that the polymerizable surfactant and the fluorinated monomer were used involved in the latex synthesis process and along with the intra- and interparticle covalent crosslinking.

L-30

SYNTHESIS OF NOVEL BIO SOURCE POLYMERIZABLE COATING PRECURSORS BASED ON DEPOLYMERIZED POLY LACTIC ACID (PLA)

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Coatings based on various polymers are used in numerous applications. Macromolecular coatings mix with additional plasticizers or additives serve their purpose in microelectronics as a permeable or semi permeable layers providing particular properties to form sensors for example.¹ Polymer materials replaced sugar or protein based coatings in pharmaceutical or medicinal industry as well.² Various protective layers are important for large scale of paper and cellulose applications. They provide a protection against flammability, humidity or general reactivity.³

Poly lactic acid (PLA) as a bio source and compostable polymer serves a lot of application. Besides of its usage for coating purposes its properties are valued in medical/biomedical industry, food packaging industry, agriculture or automotive and 3D printing. Many of these segments require PLA in a specific grade or quality and separate inappropriate polymer from their technologies.⁴

This work is focused on the synthesis of low viscosity bio source polymerizable precursors for various coating applications. At first, methyl and ethyl esters of lactic acid are prepared via alcoholysis of PLA in high temperature and pressure conditions without any solvent. The conditions for depolymeration were: temperature of 151 °C and the vapor pressure of 8,2 bar for ethyl lactate and 12,5 bar for methyl lactate. The conversions were analyzed via LC-MS and measured values were above 98 % for both esters after 2 hours. Second step of the synthesis was the methacrylation of the hydroxyl functional groups of the esters. Methacrylic anhydride (MAA) was used as a nucleophile and an innovative catalyst – potassium 2-ethylhexanoate – was chosen for the reactions. The conversions of polymerizable products reached values between 85-91 % after 5 hours of the reaction analyzed by GC-FID. All product structures were determined via methods: MS-spectrum, ¹(H) NMR and FTIR.

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L-31

LAURATE MODIFIED LOW-MOLAR-MASS SODIUM HYALURONAN ASSOCIATION AND SOLUBILIZATION EFFICIENCY IN AQUEOUS MEDIA

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A low molar mass (15000 g/mol) sodium hyaluronan (HA) was partly acylated with lauroyl groups by using the methodology of mixed anhydride acylation in aqueous organic solvents (1:1 by volume). Enzymatic degradation-based structural analyses showed no significant differences in substitution patterns of derivatives prepared in the presence of different organic co-solvents, in contrast to the results obtained earlier for both oleoyl and lauroyl hyaluronans.^{1,2} In purely aqueous solutions, lauroyl hyaluronans spontaneously formed colloidal particles of hydrodynamic diameters of the order of 10^2 nm. For example, the derivative prepared in aqueous 1,4-dioxane (HA_{LA-Diox}) formed relatively well-defined colloidal particles with hydrodynamic diameters from 200 to 400 nm. However, when dissolved in saline (aqueous NaCl, 9 g/L), the derivatives formed colloidal particles with hydrodynamic diameters smaller than 80 nm. A pyrene solubilization efficiency (measured by fluorimetry) in saline was found to be 3 to 8 times higher than in the aqueous solution of the same derivative. This difference can be explained by the increased ionic strength of the solution, which decreases intra-chain electrostatic repulsions of charged monomeric units, thus reducing the chain backbone stiffness.³

Slightly different properties of HA lauroyl derivatives prepared with different organic co-solvents can be explained by the kinetics of acylation reaction resulting in some differences in the distribution of extent of acylation between derivative macromolecules.

Solutions of all prepared HA derivatives at concentrations up to 1 g/L were found to be non-cytotoxic.

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CHANNELS WITH HELICAL MODULATION DISPLAY STEREOSENSITIVITY FOR CHIRAL SUPERSTRUCTURES

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By means of coarse-grained molecular dynamics simulations, we explore chiral sensitivity of confining spaces modelled as helical channels to chiral superstructures represented by polymer knots. The simulations show that helical channels exhibit stereosensitivity to chiral knots localized on linear chains by effect of external pulling force and also to knots embedded on circular chains. The magnitude of the stereoselective effect is stronger for torus knots, the effect is weaker in the case of twist knots, and amphichiral knots do exhibit no chiral effects. The magnitude of the effect can be tuned by the so-far investigated radius of the helix, the pitch of the helix and the strength of the pulling force. The model is aimed to simulate and address a range of practical situations that may occur in experimental settings such as designing of nanotechnological devices for the detection of topological state of molecules, preparation of new gels with tailor made stereoselective properties, or diffusion of knotted DNA in biological conditions.

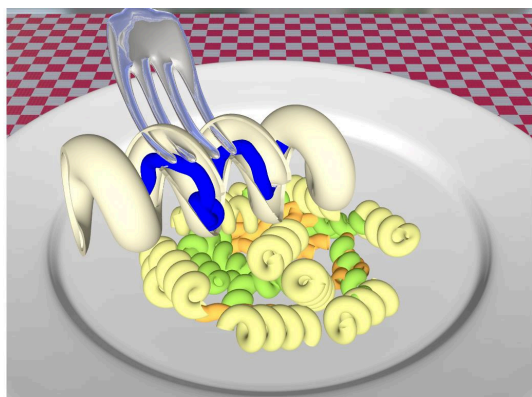


Figure 1 An artistic view on a knotted DNA confined in a helical nano-channel. Knots on DNA (chiral superstructures) occur naturally but can be induced by single molecular manipulation. Helical channels can be prepared in a form of gels, resins or molecular sieves and can make devices for emerging field of chiral nanotechnology.

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Acknowledgement: This research was funded by the Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic, Grant VEGA 2/0102/20 and Slovak Research and Development Agency SRDA 21-0346. Support from international cooperation projects COST 17 139 EUTOPIA (EUropean TOPOlogy Interdisciplinary Action) and SRDA SK-AT-20-0011 are also acknowledged.

Abstracts of Posters

P-01

SYNTHESIS AND SPECTRAL STUDY OF ASYMMETRIC THIAZOLO[5,4-D]THIAZOLE BASED MOLECULES WITH 1,3,4-OXADIAZOLE LINKER FOR ELECTRONIC APPLICATION

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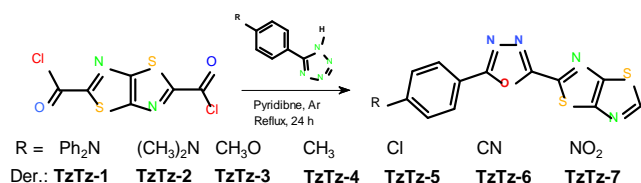
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Thiazolo[5,4-*d*]thiazole (TzTz) is a planar heterocyclic compound with rigid structure, electron acceptor properties and good stability.^{1,2} Application of derivatives of TzTz was intensively investigated in electronics such as photovoltaics, organic light emitting diodes and field effect transistors.³ However, countless symmetric TzTz based molecules were presented for electronic application with impressive properties, their asymmetric analogs attracted significantly less attention



Scheme 1. Synthesis of asymmetric TzTz compounds.

In this work we present the synthesis of seven asymmetric compounds with TzTz unit as acceptor, 1,3,4-oxadiazole as linker and with different phenyl-based electron donor (Ph₂N-, (CH₃)₂N-, methoxy, tolyl) and electron acceptor (Cl-, CN-, NO₂-) moieties (Scheme 1). The presented

derivatives were studied by UV-Vis and emission spectroscopy in chloroform, cyclic voltammetry (CV) in acetonitrile and theoretical calculations by B3LYP. Theoretical calculations showed almost perfect planarity. Using spectral data optical energy gap (E_g) (2.48 – 3.02 eV), fluorescence quantum yield (10 – 37 %) and Stokes shift (3327 – 5985 cm⁻¹) was obtained. Energies of LUMO orbitals were found between -3.19 and -3.40 eV. TzTz compounds with strong electron donor moieties on the phenyl ring showed intramolecular charge transfer (ICT) purple and blue light absorption, low band gap and. Derivatives with strong electron acceptor units showed absorption in purple and ultraviolet region without ICT and wide band gaps (3.08 – 3.70 eV).

Acknowledgement: This work was supported by the Slovak Grant Agencies: VEGA 2/0168/21 and APVV-19-0338.

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P-02

AMPHIPHILIC BLOCK COPOLYMERS AS NANOMEDICINES FOR EFFICIENT TREATMENT OF RESISTANT TUMORS

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The major cause of insufficient efficacy of antitumor therapy based on low molecular weight (LMW) cytostatics (doxorubicin etc.) is so-called multidrug resistance (MDR). Overexpression of ATP-dependent efflux pumps based on ABC transporters (in particular P-glycoprotein, P-gp) in cancer cells is often associated with emergence of MDR. Consequently, the cytostatic drug is prematurely eliminated from the organism without achieving a significant therapeutic effect. A promising solution of this problem may be use of P-gp inhibitors that should increase retention of the cytostatics inside the tumor cells, thus overcoming MDR and resulting in a more efficient antitumor therapy. Besides the LMW substances such as ritonavir or reversin also high molecular weight (HMW) poly(propylene oxide) (PPO) is described as a P-gp inhibitor. However, its use in biological systems is significantly limited by its strongly hydrophobic character. Nevertheless, its water solubility can be improved by binding to a water-soluble polymer carrier based on the well-known copolymer *N*-(2-hydroxypropyl)methacrylamide (PHPMA). Conjugation of PPO to PHPMA enables controlled delivery of the resulting macromolecular inhibitor to tumors while simultaneously reducing drug serious side effects.

We designed and synthesized a water-soluble polymer drug conjugate carrying in its structure both a cytostatic drug (doxorubicin) and a P-gp inhibitor (represented by HMW PPO). We investigated the relationship between the detailed structure of various block amphiphilic copolymers PHPMA-PPO and their efficiency of overcoming MDR through the inhibition of P-gp.

Self-assembly of the amphiphilic block copolymers into supramolecular structures (micelles) in aqueous media leads to their preferential accumulation in tumor tissue due to so-called enhanced permeability and retention (EPR) effect. Exclusion of the copolymers from the body is ensured by the micelle disintegration into unimers (with a size below the limit of glomerular filtration). The prepared copolymers were characterized by size-exclusion chromatography, dynamic light scattering, field flow fractionation and UV-VIS spectroscopy and by both in vitro and in vivo biological evaluation. Based on the results, we can conclude that the presented micelle-forming copolymers and their conjugates with doxorubicin are promising candidates for treatment of MDR tumors, for which traditional chemotherapy is not satisfactory.

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SYNTHESIS OF NOVEL BIO-BASED POLYMER GELS AND THE EVALUATION OF THEIR SWELLING PERFORMANCE

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Series of bio-based polymer gels from α -methylene- γ -butyrolactone (MBL), a biomass-derived monomer; and its co-polymer with isoprenyl oxazoline (iPOx), a biologically active monomer, were prepared *via* subsequent radical polymerization and crosslinking reaction (Figure A).¹ The crosslinking reaction was performed in solution with diamine-based compounds through selective ring-opening amidation of the pendant lactone rings. The PMBL-based gels were then examined with respect to their swelling properties and stimuli-responsive character. The physical and chemical properties of the polymer gel structures substantially influence their swelling properties. The gels also exhibited multiple external stimuli-responsive behaviours. Hence, such gels embody materials with highly tunable swelling performance. Furthermore, a model-driven analysis using equilibrium swelling theory was performed to investigate the gel network structure-swelling dynamic relationship. (Figure B).² The overall research findings offered insight into the effect of the design parameters on the swelling properties of the pMBL-based gels vital for their biomedical and electronic applications.

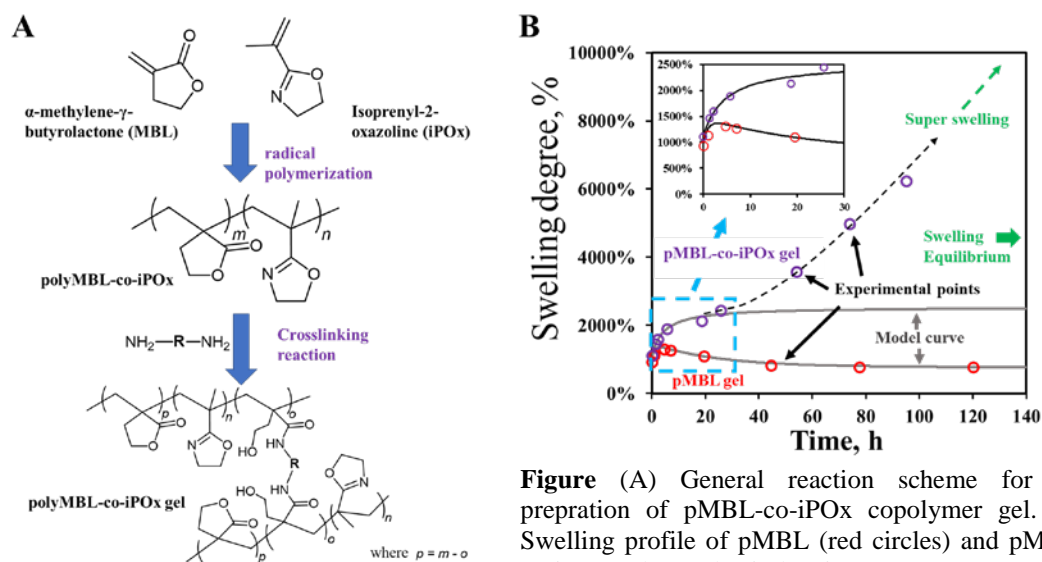


Figure (A) General reaction scheme for the preparation of pMBL-co-iPOx copolymer gel. **(B)** Swelling profile of pMBL (red circles) and pMBL-co-iPOx gel (purple circles) in DMSO, 25°C.

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P-04

LOW-DENSITY SEMI-RIGID POLYURETHANE FOAMS BASED ON BIO-BASED POLYOLS

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Recent sustainable chemistry concept has promoted investigations using various renewable resources for the synthesis of novel bio-based polyurethanes (PUs). The production of polyols from different renewable resources (vegetable oils, microalgae, lignocellulose, and polysaccharides) has been widely studied.¹ Among all accessible environment-friendly feedstocks, succinic acid (SA) has been found to be a suitable raw material for polyol synthesis.² SA-based polyols can be employed in the preparation of different groups of polyurethane materials, one of them being rigid foams. Rigid PU foams are currently one of the most used materials in the construction industry. They have excellent insulation properties which come from a low thermal conductivity and a closed-cell structure.³ Up until recently, not much research was done on open-cell rigid and semi-rigid foams but in past years they started gaining scientific interest. A great advantage of open-cell foams over closed-cell ones is their lower apparent density resulting in a lower price and material savings. Due to their small pore size, low thermal conductivity, and good moisture permeability they can be considered as a new type of thermal insulator. Moreover, these foams thanks to their enhanced damping properties, can be good sound- and vibration-absorbing materials.^{3,4} In this study, a series of bio-based polyester-ether polyols of different functionality based on SA and tetraethylene glycol were prepared. The obtained polyols were applied for the preparation of semi-rigid PU foams exhibiting very low density without occurring adverse foam shrinkage. Moreover, the produced PU foams have homogeneous and partially opened cellular structure, good mechanical and thermal properties. In conclusion, the results showed that SA acid is a promising renewable alternative to petrochemical feedstock for PU foams.

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MODIFIED MAGNETIC POLYMER COMPOSITES FOR BIOMEDICAL APPLICATIONS

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The wide variety of nature-derived and synthetic polymers and numerous techniques of their processing make polymers the leading materials for development of scaffolds in tissue engineering applications. Nevertheless, their modification with additional active compounds is required to enhance specific properties, like mechanical strength, reduced inflammation, stimulation of cell proliferation, etc.¹

Herein, poly(ϵ -caprolactone) (PCL)-based fiber nanocomposites modified with iron oxide nanoparticles (IONs) and antioxidant agent L-ascorbic acid (LAA) were fabricated via an electrospinning method. The IONs ($D_n = 10$ nm) were synthesized by coprecipitation and grafted with PCL to provide their good distribution within the polymer matrix. A series of composites with 2 wt.% of modified IONs and various contents of LAA (1, 2, 5, and 10 wt.%) was prepared. The effect of increasing content of LAA in nanocomposites on their morphology, mechanical and magnetic properties, release of antioxidants, and biological response towards SAOS-2 cell were evaluated. The SEM micrographs illustrated typical smooth morphology of fibers. Up to 2 wt.% of LAA, the fiber diameters decreased with increasing content of LAA. At higher LAA contents, the fiber diameter did not change. High contents of LAA (5 and 10 wt.%) enhanced the mechanical properties of nanocomposites, i.e., Young's modulus and tensile strength. LAA was released after 10 days of incubation in water at 37 °C. The developed nanocomposites were non-toxic toward SAOS-2 human osteosarcoma cells. The metabolic activity of cells was time-dependent; however, the distinct correlation between the content of LAA and cell viability was not observed.

The modification of PCL matrix with antioxidant and magnetic nanoparticles enabled to obtain multifunctional scaffolds for tissue engineering. The LAA content modulated the morphology and mechanical properties of the composites, but did not affect SAOS-2 cell response toward nanocomposites.

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P-06

SYNTHESIS OF HYBRID POLYMER MATERIALS FROM POLY(2-OXAZOLINE)S AND POLYPHOSPHAZENES

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This work was focused on the synthesis of new hybrid polymer systems comprising biocompatible poly(2-oxazoline)s and biodegradable polyphosphazenes suitable for various biomedical applications. Poly(2-oxazoline)s represent a promising type of biomedical grade polymers for different biomedical applications. They have been used as various drug and gene delivery systems, hydrogels, 3D bioprinting materials, or tissue engineering applications.¹ From the plethora of 2-oxazoline based polymers, poly(2-isopropenyl-2-oxazoline) (PIPOx) represents a universal platform for the preparation of biomaterials for various biomedical applications.² Pendant 2-oxazoline groups allow to introduce in post-polymerization modifications of different moieties.

One of the main drawbacks of PAOx is their low biodegradability. Therefore, molecular hybrid materials of PAOx with other biodegradable materials are in high demand. Polyphosphazenes (PPz) are well-reported to undergo hydrolytic degradation to a benign, pH-neutral mixture of phosphates and ammonium salts.³⁻⁵ Furthermore, the degradation rate can be simply tuned by controlling access of H₂O to the main chain phosphorus; thus, a range of degradation rates are readily accessible.

PIPOx was prepared using aqueous ATRP resulting polymer with a molar mass of 18000 g.mol⁻¹ and polydispersity of 1.23. PPz was prepared in multistep polymerization, and the carboxy end-group was introduced by a thiol-ene click reaction with thioglycolic acid. Hybrid materials have been prepared by post-polymerization reaction of 2-oxazoline rings from PIPOx with carboxy end-groups of PPz in three different molar ratios. The structure of prepared hybrid polymers was determined by NMR and FTIR spectroscopies. Molecular characteristics were measured by GPC.

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PEGYLATED IRON/CERIUM OXIDE NANOPARTICLES WITH MAGNETIC AND ANTIOXIDANT PROPERTIES

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Superparamagnetic γ -Fe₂O₃/CeO₂ nanoparticles with enzyme-mimicking antioxidant properties were obtained by basic coprecipitation of iron chlorides followed by oxidation with hydrogen peroxide and precipitation of Ce(NO₃)₃ with ammonia. The formation of CeO₂ seeds on the magnetic particle surface was confirmed by transmission electron microscopy, EDX and XPS spectroscopies, powder X-ray diffraction, dynamic light scattering, and elemental analysis.^{1,2} Determination of γ -Fe₂O₃/CeO₂ magnetic properties on a vibrating magnetometer confirmed their superparamagnetic nature. The surface of particles was functionalized with poly(ethylene glycol)-neridronate (PEG-Ner) of two different molecular weights to ensure colloidal stability and biocompatibility. Chemical and *in vitro* biological assays proved that the nanoparticles, due to the presence of cerium oxide, effectively scavenged radicals. Thus, levels of oxidative stress decreased in the model U87MG human glioma cells incubated with the nanoparticles.¹ PEG-Ner functionalization of the nanoparticles diminished their *in vitro* aggregation and facilitated lysosomal degradation in cancer cells during autophagy, which resulted in concentration-dependent cytotoxicity of the nanoparticles. Moreover, their ability to affect oxidative stress in hereditary hypertriglyceridemic rats was tested by biological tissue assay of the liver, kidney cortex, and brain.² An improvement was observed in both enzymatic and non-enzymatic levels of antioxidant defense and lipid peroxidation parameters. The results corresponded with chemical determination of antioxidant activity, proving that the studied nanoparticles effectively scavenged radicals due to the presence of cerium oxide, which decreased oxidative stress in the animal model. The particles may therefore have the potential to reduce disorders associated with oxidative stress and inflammation; at the same time, they are traceable by magnetic resonance imaging.¹

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P-08

DWELLING INTO POLYUREA AMBIENT-CURE PROTECTIVE COATINGS: CHARACTERIZATION OF FILM FORMING PROPERTIES AND DEPTH-DEPENDENT CURING

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Protective coatings are indispensable for maintaining the integrity of surfaces and extending the service life of objects, by reducing materials damages caused by weathering, exposure to chemicals, mechanical failure, etc. Recently introduced polyurea coatings based on aspartate esters provide layers with high hardness, short curing time, excellent chemical, moisture, and wear resistance while relatively long pot life. The polyaspartic coating is synthesized through a condensation reaction of aspartate precursors – the structure bearing secondary amine groups – and the polyisocyanates. The coatings are formed by simultaneous and interdependent physical drying and chemical crosslinking accompanied by the passage of the system through its glass transition region thus leading to a gradient of properties. To control the gradient formation and be able to suppress the solvent entrapment is a long-standing endeavor of the coating formulators and the aim of this study.

We introduce the in-house synthesized aspartate esters of varied chemical structures via aza-Michael addition, and the study of formation of the high solid solvent-borne polyurea coatings from these aspartates. PUs are formed by in-situ crosslinking of the two-component high-solids (≥ 60 wt.-%) under ambient conditions without the option of the baking stage. The structural and chemical changes occurring within the forming layer were studied by depth-dependent Raman confocal microscopy. We were able to track the formation of bound vs. free urea bonds as a function of the film depth and time. We will show that these gradients may contribute to the film's early integrity and will show parameters influencing the gradient formation. At the same time, the gradient may cause severe entrapment of solvent and should be controlled. To achieve the gradient control, the film formation process and the effects of parameters must be thoroughly investigated.

The forming PU coatings were characterized by DSC, FT-IR, micro- and nano-indentation. We link the effect of the aspartate unit chain with the film drying rate and the hardness build-up. Additionally, the effect of the reaction by-products formed during amine-isocyanate curing will be elucidated.

Keywords: polyurea, coating, aspartate ester binder, polyaspartic coating, high-solid coating

THE INFLUENCE OF CLAY DISPERSION PH ON THE MECHANICAL PROPERTIES OF THE NANOCOMPOSITE HYDROGELS

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Self-assembled nanocomposite hydrogel based on Laponite nanoparticles and high molecular weight (HMW) polyelectrolyte is a promising material that exhibits excellent mechanical and superabsorbent properties as well as self-healing behaviour due to ionic interactions between clay nanoparticles and ionized groups of the polyelectrolyte chain.¹ Two COO⁻ per each monomer unit make HMW poly(itaconic acid), synthesized by our new method,² a suitable polyelectrolyte for the preparation of these physical hydrogels. Another advantage of these hydrogels is their easy and quick preparation by mixing an aqueous Laponite nanodispersion containing a phosphate dispersant and an aqueous polyelectrolyte solution. It is well known that the molecular weight of the polyelectrolyte, the content of clay nanoparticles, and the concentration of the dispersant strongly affect mechanical properties. However, another key factor - the pH effect of Laponite dispersion has not been studied so far. Since a positive charge is formed due to the dissociation of -OH groups on the edge of the Laponite particles, pH>7 is a consequence of this phenomenon. A decrease in pH promotes the further release of OH⁻ anions and thus increases the number of positive charges on the edge of each clay particle.³ However, according to Jatav,⁴ lowering the pH below 9 leads to clay dissolution. Therefore, this study aims to understand better the changes in the ionic interactions of this nanohydrogel, and consequently, its mechanical properties, induced by lowering the pH. Although previous research has shown the optimum pH of the medium to be between 9 and 11⁴, we sought to determine, by examining rheological, SAXS, and NMR measurements, whether the use of a phosphate dispersant would allow further pH lowering and the subsequent improvement of the nanohydrogel's mechanical properties. Our rheological results indicated that lowering the pH to 8 leads to an increase in the hydrogel's structural strength and the extension of its linear viscoelastic region. The SAXS results showed that the pH of the Laponite dispersion must be higher than 7 to avoid the aggregation of the clay particles and NMR indicated that the highest mechanical strength of the hydrogel at pH=8 of the dispersion was not related to the content of immobilized anions (ca. 50%), but it was a result of stronger screening of the rest of the phosphate anions and thus, a wider range of the Laponite-phosphate interactions.

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P-10

POLYMER THERAPEUTICS AND DIAGNOSTICS TARGETED WITH RECOMBINANT ANTIBODY FRAGMENTS

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Conjugates of hydrophilic polymers with cytostatic drugs offer numerous advantages in treatment of malignancies compared with the low-molecular weight cancerostatics. The polymer conjugates generally exhibit higher solubility, prolonged blood circulation and increased accumulation in solid tumors. Choice of a specific targeting ligand can further increase the therapeutic potential of the polymer-drug conjugates. Among the numerous targeting ligands described in literature, antibodies and antibody fragments belong to the most efficient ones. However, well-defined covalent attachment of a complex protein molecule to a multivalent polymer carrier represents quite a difficult synthetic task. Therefore, we have been investigating various covalent and non-covalent methods of polymer protein conjugation.

First, we have developed an anchoring system based on formation of a coiled coil heterodimer between two complementary peptide sequences. One peptide was covalently attached to a synthetic hydrophilic copolymer based on *N*-(2-hydroxypropyl)methacrylamide (HPMA) bearing also a cytostatic drug doxorubicin; the second peptide was incorporated to the C-terminal part of a recombinant single chain antibody fragment of anti-GD2 monoclonal antibody.¹ Later, we have developed a non-covalent protein-polymer anchor that utilized strong non-covalent interaction between His-tagged recombinant protein and tris(nitrilotriacetic acid) chelating group attached to HPMA-based copolymer.² Most recently, we have prepared a covalent polymer-protein conjugation system utilizing sortase A-catalyzed coupling³ of recombinant antibody fragment containing peptide LPETG to a polymer bearing *N*-terminal triglycine sequence.

The antigen-specific cell binding and cytotoxicity of all systems were investigated and compared with analogous non-specific covalent polymer-protein conjugates.

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HYDROPHILIC POLYMER-PIRARUBICIN CONJUGATES FOR CANCER TREATMENT

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One of the main limitations of numerous low molecular weight cytostatic drugs is their non-specific biodistribution leading to severe adverse effects on healthy parts of the organism during cancer treatment. A possible solution is use of biocompatible polymer drug carriers that enable passive tumor accumulation.¹ In recent decades, *N*-(2-hydroxypropyl) methacrylamide (HPMA) copolymers were introduced as efficient drug carriers intended for delivery and controlled release of anticancer drugs in tumor tissue.² Nevertheless, for higher loading of very hydrophobic moieties, HPMA-based drug carriers could be insufficient; therefore, demand for new highly hydrophilic and non-fouling polymers is obvious. Moreover, slightly acidic tumor microenvironment caused by glycolytic cancer cell metabolism enables pH-dependent release of the cancerostatic drug from the polymer scaffold.

The hydrophilic character of the polymer backbone together with the optimal rate of the drug release are essential to achieve the maximal antitumor effect, which is highly dependent on the spacer architecture. In this work, we focused on the development of highly water-soluble polymer carriers based on *N*-(1,3-dihydroxypropyl) methacrylamide (DHPMA).³ Conjugates of DHPMA or HPMA copolymers with an anticancer drug pirarubicin bound through a pH-sensitive hydrazone bond were synthesized. Moreover, with the intention to study the rate of drug release, the drug was bound via three different spacers differing in the length.

Considering the observed results, we are convinced that the novel highly hydrophilic polymer drug conjugates have a great potential as efficient drug delivery systems.

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CARBON BLACK COMPOSITES VIA STEREOLITHOGRAPHY

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3D printing has recently expanded into various areas including research, rapid prototyping, and small-scale production. To meet the rapidly increasing application requirements, the materials with tailored properties are a basic prerequisite. In this work, we modified photopolymerizable resin by addition of carbon black filler in various concentrations and characterized final properties of composites prepared by stereolithography 3D printing technique. The maximum amount of carbon black (3 wt%) was limited due to the low adhesion to the printing platform. Such a low adhesion was explained by decreased transmittance with increased filler content as shown by UV-VIS spectrometry. Mechanical analyses showed decrease in glass transition temperature and Young's modulus with increasing filler content. The higher filler content also increased the amount of unreacted monomer within the bulk of composite as suggested by differential scanning calorimetry. The resistivity of composites was lowered by introduction of carbon black, however, percolation threshold was not reached. Interestingly, the addition of 0.5 and 1 wt% of carbon black had almost no impact on dielectric number, while its value almost doubled upon adding 3 wt%.



Figure 1: Samples for tensile test

Acknowledgement: This work was supported by the Grant Agency of the Czech Technical University in Prague (grant no. SGS22/054/OHK3/1T/13) and the University of Chemistry and Technology Prague.

POLY(2,3-DIHYDROXYPROPYL METHACRYLATE)-COATED UPCONVERTING NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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Lanthanide-doped upconverting nanoparticles (UCNPs) represent a novel class of light-emitting materials. The unique and outstanding properties of UCNPs, such as converting lower-energy photons into higher ones by anti-Stokes shift, tunable excitation range, sharp emission bands and low background, low photodamage to biological tissues, and deep tissue penetration depth of excitation light, make them a perspective material for various bioapplications, e.g., bioimaging, drug and gene delivery, and photodynamic therapy of cancer. However, there are a few disadvantages of neat UCNPs that limit their applications in biomedicine: particle aggregation in buffers and biological fluids and “dark toxicity” due to leakage of lanthanide and fluoride ions coming from particle degradation. Thus, the development of surface-modified UCNPs with excellent colloidal and chemical stability is crucial to overcome the above-mentioned negative effects and use these materials in different theranostic applications.¹

The aim of work was to prepare poly(2,3-dihydroxypropyl methacrylate)-coated UCNPs via a reversible addition-fragmentation transfer (RAFT) miniemulsion polymerization. Hence, the uniform UCNPs were synthesized and coated with hydrophobic penta(propylene glycol) phosphate methacrylate (SIPO) to reduce the ion leakage and increase the reactivity exploitable in the miniemulsion polymerization. The poly(glycidyl methacrylate) (PGMA)-coated multicore UCNPs were synthesized via a miniemulsion RAFT polymerization of glycidyl methacrylate in the presence of UCNPs. Pre-synthesized poly(2,3-dihydroxypropyl methacrylate)-based macroRAFT agent was used as a surfactant and chain transfer agent. The amount of polymer on UCNP surface and the size of the nanoassemblies were controlled by adjusting of synthesis parameters. The hydrophobic PGMA shell is suitable for the incorporation of theranostic agents including drugs photosensitizers and dyes, and it can be further transformed in a hydrophilic shell by hydrolysis for *in vivo/in vitro* bioapplications (e.g., cell and tissue imaging).

The developed surface-modified multicore-shell UCNP nanoassemblies with size ranging 120-500 nm were characterized using dynamic light scattering, fluorescent emission spectroscopy, and transmission and scanning electron microscopy. The presence of polymer layer on the particle surface was confirmed by FTIR spectroscopy and thermogravimetric analysis.

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Acknowledgement: This work was supported by the Czech Science Foundation (21-04420S).

pH-RESPONSIVE GIANT UNILAMELLAR VESICLES

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Recently, there has been a growing interest in the formation of polymer-lipid hybrid self-assemblies (herein named, hVS), which allow combining and improving the main features of pure lipid-based and copolymer-based assemblies known for their potential applications in the biomedical field.¹ The hVS are capable of accommodation of hydrophobic compounds in their membrane and hydrophilic agents in their aqueous lumen. They become particularly interesting and subject of high attention because their size is comparable to that of eukaryotic cells, thus being used for creating biomimetic vesicles.³ In addition, their size allows for the use of conventional fluorescent microscopy techniques, enabling their interactions with proteins and/or communication with cells to be readily visualized. Herein, we present monodisperse pH-responsive giant hVS by using the electroformation method. Several lipids/polymer ratios were tested using the pH-responsive homopolymer poly[2-(diisopropylamino) ethyl methacrylate]-synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization post-conjugated to cholesterol and used in combination with poly(1,2-butadiene)-*b*-poly(ethylene oxide). The pH-responsive behavior was studied in detail by confocal microscopy and the results demonstrated the spatial and temporal pH-controlled hVS disruption under simulated relevant physiological conditions. This approach can be utilized to fabricate pH-responsive delivery systems for several active compounds, microreactors, and artificial organelles toward cell mimicking.

Acknowledgments: The authors gratefully acknowledge financial support from the Czech Science Foundation (grants no. 20-15077Y and no. 20-13946Y).

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