SILESIAN MEETINGS ON POLYMER MATERIALS

POLYMAT

2022

ORGANIZED BY

POLISH ACADEMY OF SCIENCES

CENTRE OF POLYMER AND CARBON MATERIALS

ZABRZE, 17 MARCH, 2022

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The Silesian Meetings on Polymer Materials

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The third edition of the international conference Silesian Meetings on Polymer Materials POLYMAT has a unique character – it is an opportunity o commemorate Prof. Andrzej Dworak, an undisputed authority in the field of polymer chemistry and polymer materials. A special session inaugurating the POLYMAT2022 conference is devoted to prof. Andrzej Dworak, an extremely creative person, appreciated by the polymer community, co-founder of the fame of the Centre of Polymer and Carbon Materials of the Polish Academy of Sciences (CMPW PAN) in Zabrze

Prof. Andrzej Dworak (1945-2021) – chemist, excellent scientist, long-term director of the CMPW PAN (2007-2019). He was an outstanding specialist with experience in studies of the mechanisms of oxirane and cyclic imines polymerization and controlled radical polymerization of various types of monomers in order to obtain macromolecules with carefully planned structure and properties, including polymers sensitive to stimuli. These studies have opened the way to the use of such polymers for the construction of nanomaterials that can be applied in medicine and pharmacy. Prof. Dworak published more than 150 works in the international journals, he was also a co-athor of several patents. He was a coordinator of many national and European projects, carrying out works both in the field of basic research, as well as with implementation potential.

Andrzej Dworak was also professor at the Faculty of Chemistry at the University of Opole. He transferred a knowledge of the polymer chemistry and polymer materials, especially for medical and pharmaceutical applications. He was able to share his enormous knowledge and inspire others with it. He raised many generations of young chemists, many of whom continue his scientific passion.

Prof. Dworak was very active as an organizer of science. He initiated the conference "The International Polymer Seminar in Gliwice", where he was the chairman in the years 1995-2008. He was the organizer and chairman of the international conferences Polimery nad Odrą POLYOR2011 in Opole and the Silesian Meetings on Polymer Materials – POLYMAT60 and POLYMAT2016 in Zabrze. He was the initiator and the coordinator of the first in Poland European PhD Study "Modern polymer materials". As a long-term member of the Polish Chemical Society, he was the chairman of the Gliwice Branch of PTChem and the Polymer Section of PTChem, and from September 2016 he was the vice-chairman of the Polish Chemical Society. In 2016-2018 he was a representative of Polish polymer chemists in the European Polymer Federation. He was a member of the Committee Chemistry of the Polish Academy of Sciences, the Scientific Council of the Centre for Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź, a member of the Program Council of the Polimery journal. As a recognition of the Professor's scientific position and the result of his many years of cooperation with the Institute of Polymers of the Bulgarian Academy of Sciences he was chosen for a foreign member of the Bulgarian Academy of Sciences in 2017. Professor Dworak was also an expert and reviewer at the National Science Center and the National Centre for Research and Development. He was a permanent reviewer of many important polymer magazines. He reviewed many doctoral dissertations, habilitation theses and professor's applications.

Prof. Andrzej Dworak devoted his entire life to science, science was also his passion. He was an outstanding scientist, but he will remain in our memory as a great supervisor, colleague and friend. His memory will continue in the works of his students, he will live in the grateful memory of many colleagues from Poland and abroad.

PROGRAM

Thursday, March 17, 2022

7:30	Registration	
9:15-9:30	Opening *Prof. Janusz Jurczak* Chairman of the Committee of Chemistry Polish Academy of Sciences, Warsaw, Poland	**Chairman:** *Prof. Marek Kowalczuk*
9:30-9:45	*Prof. Zbigniew Florjańczyk* Warsaw University of Technology, Poland	In memory of the work and scientific activity of prof. A. Dworak
		Chairman: *Prof. Stanisław Słomkowski*
9:45-10:00	*Prof. Stanisław Penczek* Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland	In memory of the work and scientific activity of prof. A. Dworak
10:00-10:45	*Prof. Axel Müller* Johannes Gutenberg University Mainz, Germany	"Tapered block and multiblock copolymers via statistical anionic copolymerization"
10:45-12:00	Coffee break with poster session	
		Chairman: *Prof.Christo Tsvetanov*
12:00-12:45	*Prof. Rainer Haag* Freie Universität Berlin, Germany	"Multifunctional Polyglycerols Synthesis and Biomedical Applications"
12:45-13:30	*Prof. Stergios Pispas* National Hellenic Research Foundation, Athens, Greece	"Thermoresponsive linear and hyperbranched copolymers using RAFT polymerization"
13:30-15:00	Lunch with poster session	
		Chairman: *Prof. Hans-Juergen Adler*
15:00-15:45	*Prof. Petar Petrov* Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria	"Multifunctional block copolymer nanocarriers"
15:45-16:30	*Prof. Brigitte Voit* Leibniz Institute of Polymer Research, Dresden, Germany	"Responsive nanocapsules and multicompartments as cellular mimics"
16:30	Best poster award Closing remarks with farewell toast	

POLYMAT 2022 BEST POSTER AWARDS GRANTED BY POLYMERS MDPI

CATHEGORIES:

Best Poster Presented Within The Field of Advanced Polymeric Biomaterials

Best Interdisciplinary Work In The Framework of Cooperation Between Scientific Institutions

Best Poster In The Field of Advanced Techniques of Synthesis And Characterization of Polymeric Materials

Poster Award Committee will review the posters presented at the Poster Sessions during the Conference. Selections will be based on the importance of the research, quality of the poster, and clarity of the presentation.

List of contributions

List of posters

ABSTRACTS OF INVITED LECTURES

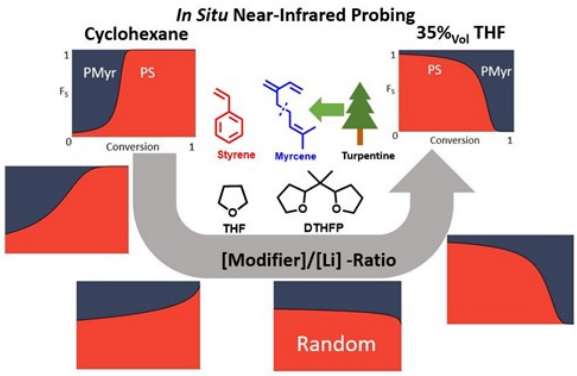
L-1

Tapered block and multiblock copolymers of styrene and dienes via statistical anionic copolymerization

Axel H. E. Müller, Marvin Steube, Tobias Johann, Dominik Fuchs, Thi Dinh, Holger Frey

Department of Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany

The statistical anionic copolymerization of styrene (S) with dienes (butadiene, isoprene) with lithium counterion in apolar solvents is commonly used to synthesize “tapered” block copolymers, enabling the control of the phase behavior by adjusting the order-disorder transition temperature. Recently, biobased terpene derivates like β-myrcene or β-farnesene have come into the focus of interest. Lewis-base modifiers (ethers, amines) have been used to “randomize” the copolymerization, also affecting the stereostructure of the polydiene comonomer segments.



The effect of THF and other (mono- and multidentate) ethers on the copolymerization kinetics of styrene with isoprene and myrcene, respectively, and the gradient of the resulting copolymers were systematically investigated by increasing the [modifier]/[Li] ratio). *In situ* near-infrared (NIR) spectroscopy was employed as a versatile and fast method to track the highly accelerated consumption of the individual monomers. Reactivity ratios were determined as a function of the [THF]/[Li] ratio. They revealed a gradual reversal from $r_{diene} >> r_S$ over $r_{diene} \approx r_S$ to $r_{diene} << r_S$. Corresponding changes in the copolymer composition profile up to a complete inversion are evident in thermal properties and morphologies. Although all copolymers possess the same comonomer composition (57%$_{vol}$ PS-units) small-angle X-ray scattering and transmission electron microscopy give evidence of a wide variation in bulk morphologies depending on the gradient profile. Overall, the phase diagram is symmetric and the succession of phases bears certain similarities to the corresponding block copolymers. The degree of segregation as well as the nanodomain structure control the mechanical properties, showing a remarkably different viscoelastic response either leading to hard/brittle or ductile/soft materials.

Using the knowledge obtained in the kinetic experiments we synthesized multiblock copolymers with up to ten blocks by sequential additions of the comonomer mixtures. The mechanical properties (viscoeleastic response) can be finely tuned by the judicious selection of molecular weight and number of blocks.

L-2

Linear and dendritic polyglycidols as multifunctional platform for design of broad-spectrum antiviral materials and coatings

Rainer Haag, Chuanxiong Nie, Paria Pouyan, Maiko Schulze

Institute for Chemistry and Biochemistry, Freie Universität Berlin, Germany

Polyglycerol (PG) is a biocompatible and water-soluble polymer, which is synthesized via ionic ring-opening polymerization of glycidol, that due to its structure, leads to branched architectures. Linear polyglycerol (LPG) can be synthesized by polymerization of protected glycidol monomer.[1] After the polymerization, deprotection of the backbone leads to linear structures with free hydroxy groups. Both branched and linear structures can be polymerized via different strategies namely cationic, anionic and coordination polymerization.

The biocompatibility, anti-fouling properties and multifunctionality of PG, has made it a suitable platform for introduction of different binding and targeting moieties for a broad range of applications.

Modification of PG with sulfate groups leads to heparin-mimicking structures with anti-inflammatory[2] and broad-spectrum antiviral activity which outperform heparin, while having less anticoagulant activity.[3] These polymers can be synthesized with different structures like linear, dendritic and hyperbranched[3b] or come together for making architectures such as 2D nanosheets[4] or 3D hydrogels.[3a]

Recently, our studies have shown that further modification of sulfated hyperbranched with hydrophobic alkyl chains can not only inhibit the viral infection but also irreversibly rupture the viral capsid in a way that virions are infectious anymore, a property called virucidality.[5] Furthermore, these polymers can be applied via different strategies as surface coatings to introduce antiviral or anti-fouling properties onto the target surface.

We have recently developed a robust method using UV light to covalently introduce sulfated LPG with an UV-crosslinkable anchor block onto a variety of polymeric surfaces.[6] Moreover, these polyelectrolytes can non-covalently applied using layer-by-layer coating strategy, using electrostatic forces between layer with opposite charges. These two coating methods are now under further investigation in our group to produce antiviral face masks and air filters.

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L-3

Thermoresponsive linear and hyperbranched copolymers using RAFT polymerization

Stergios Pispas

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Keywords: thermoresponsive, polymers, hyperbranched copolymers, RAFT polymerization, self-assembly

Thermoresponsive copolymers are a class of interesting macromolecules which change their conformation and aggregation state because of changes in solution temperature. They can be utilized in several biomedical applications, such as carriers of drugs and bioimaging agents, while they can be used as models for protein structure/conformation and assembly. So far, mainly linear copolymer architectures have been studied while the behavior of hyperbranched thermoresponsive copolymers is relatively unexplored. In this presentation several linear and hyperbranched copolymers containing thermoresponsive parts and synthesized by RAFT polymerization schemes will be discussed. Aspects of their solution self-assembly and co-assembly with pharmaceutical compounds, DNA and inorganic nanoparticles in aqueous media will be also illustrated.

L-4
Multifunctional block copolymer nanocarriers

Petar D. Petrov

Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria

Keywords: block copolymers, micelles, niosomes, drug carriers, nanomedicine

Multifunctional nanocarriers are being intensively studied as promising platforms to overcome some of the existing pharmaceutical and clinical limitations. This talk presents our latest contributions to the field of multifunctional block copolymer nanocarriers for (co)delivery of hydrophobic and hydrophilic substance with antitumor and antioxidant activity. The focus is on the synthesis of amphiphilic block copolymers, appropriately designed for the preparation of multifunctional (mixed) micellar and niosomal nanocarriers by (cooperative) self-assembly in aqueous media. *In vitro* experiments with nanocarriers, loaded with model biologically active substances (curcumin, caffeic acid phenethyl ester, doxorubicin), demonstrating key features of the developed systems such as controlled/triggered drug release, enhanced structural stability, high loading efficiency, pronounced antitumor and antioxidant activity as well as the potential for targeted delivery of anti-cancer drugs in mitochondria are also within the scope of this presentation.

Acknowledgments: *This study was supported by the Bulgarian National Science Fund (Grants DN 09-1/2016 and KP-06-H43/3-2020).*

L-5
Responsive nanocapsules and multicompartments as cellular mimics

Brigitte Voit

Leibniz-Institut fuer Polymerforschung Dresden, Dresden, Germany

Keywords: polymersomes, nanocapsules, pH responsive, multicompartments, cellular mimics

Polymeric micro- or nanocapsules and multicompartment systems are highly interesting in the field of nanoreactors and in mimicking biological systems and processes. Of special interest is the introduction of a stimuli-responsiveness into the capsule shell to be able to control the traffic of small and larger compounds and particles into and out from the capsule interior. We will report firstly on responsive nanoparticles based on photocrosslinked polymersomes. Larger proteinosomes (up to 20 micrometer), prepared by pickering emulsion from BSA-PNIPAAm bioconjugates have been considered as synthetic cell wall, and those compartments have been equipped with the smaller pH-responsive polymersomes, mimicking organelle structures in a cell. Examples will be giving how these multicompartments can be used to study complex cellular functions controlling cellular traffic.

ABSTRACTS OF POSTERS

1

Flame-retardant cotton fabric by oxygen-tolerant photomediated atom transfer radical polymerization

Gamal Zain[1], Igor Jordanov[2], Jaroslav Mosnáček[1]

[1]*Polymer Institute SAS, Bratislava, Slovakia, upolgaza@savba.sk*

[2]*Department of Textile Engineering, Faculty of Technology and Metallurgy, Ss. Cyril and Methodius University, Skopje, Macedonia*

Keyword: cellulose, grafting from, photo ATRP, dimethyl(methacryloyloxymethyl) phosphonate

Photomediated atom transfer radical polymerization (PhotoATRP) has received considerable attention owing to the well-established benefits including very low catalyst loading, oxygen tolerance, temporal control, and environmental benignity[1-3].

Phosphorus-containing polymers are very promising because of the versatility of their applications. Among phosphorus compounds, phosphate- and phosphonate-containing polymers have received much interest over decades. Polyphosphates and polyphosphonates are well-known for their excellent fire-retardant properties. In this work, oxygen-tolerant photoATRP of dimethyl(methacryloyloxymethyl) phosphonate (MAPC1) was first studied in solution. Then, the optimized conditions were applied for surface modification of cotton fabric to obtain Poly(MAPC1) brushes onto the surface. The "grafting from" strategy[4] was used for such modification which relies on converting the substrate to a macroinitiator first. The modified cotton fabrics were characterized by attenuated total reflection-Fourier transforms infrared spectroscopy and X-ray photoelectron spectroscopy. The results confirmed that MAPC1 monomer was successfully grafted onto the cotton fabric where the grafting percentage can be controlled by varying the polymerization conditions. The thermal properties and flammability of the modified fabrics were tested by thermogravimetric analysis, horizontal and vertical flame tests which revealed substantial flame-retardant properties represented in the char length and residual weight percentage. Furthermore, the durability of the modified fabrics will be also investigated.

Acknowledgment: *This work is supported by projects APVV-19-0338, VEGA 2/0168/21 and Context17107 action.*

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2
Lithium borohydride reduction as a method of modifying a surface of electrospun polyhydroxyalkanoate scaffolds

Paweł Chaber[a], Jakub Włodarczyk[a], Paweł Nitschke[a], Anna Hercog[a], Patrycja Tworzydło[a], Sebastian Jurczyk[b], Jakub Rech[c], Grzegorz Tylko[d], Grażyna Adamus[a]

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[b]*Institute for Engineering of Polymer Materials and Dyes, Lukasiewicz Research Network, Torun, Poland*

[c]*Department of Biotechnology and Genetic Engineering, Faculty of Pharmaceutical Sciences in Sosnowiec, Medical University of Silesia, Katowice, Poland*

[d]*Department of Cell Biology and Imaging, Institute of Zoology and Biomedical Research, Faculty of Biology, Jagiellonian University, Kraków, Poland*

Keywords: tissue engineering, polyhydroxyalkanoates, surface modification, borohydride reduction

In recent years, polyhydroxyalkanoates (PHAs), due to their properties like biodegradability and biocompatibility, have been recognized as attractive biomaterials with a significant future impact on medical practice and research. However, specific applications such as, for example, tissue engineering scaffolds require that biomaterials have a wide range of unique properties, most of which cannot be met by PHAs in their native form. Therefore, systematic research on the modification of PHA biopolyesters has been carried out recently. In this communication, we present a simple way to modify the surface chemistry of fibrous scaffolds made of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV). The method involves the use of lithium borohydride as a reducing agent and results in enriching the surface with hydroxyl groups. The presence of these groups at the material's surface significantly improves the biological performance of the scaffolds.

Acknowledgments: *This work was supported by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 872152, project GREEN-MAP.*

3
Degradable hydrogels based on cyclodextrin-polyurethane

Alexandra-Diana Diaconu, Cristian Peptu, Valeria Harabagiu

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

Keywords: cyclodextrin, cyclodextrin-oligolactide, degradable hydrogels

The objective of this study is to find out the appropriate conditions for the synthesis of cyclodextrin-polyurethane degradable hydrogels, by introducing oligolactide chains in the polymer network structure. Our approach is focused on the synthesis of polyurethane hydrogels with native and modified cyclodextrin in two stages. The first stage consisted in obtaining the cyclodextrin modified with oligolactide, by the ring-opening of D,L-Lactide. Also, this stage included the synthesis of a prepolymers based on polyethylene glycol and isophorone diisocyanate. The reaction conditions for obtaining this prepolymer were optimized using mass spectrometry (MALDI MS). In the final stage the prepolymers were crosslinked and the gelation process was further studied by rheology. The resulted hydrogels were purified and thoroughly characterized in view of their structure and morphology (FTIR, SEM), water uptake, and hydrolytic degradation.

4

Codelivery of 8-hydroxyquinoline glycoconjugates and doxorubicin with pH-responsive supramolecular hydrogel matrix for enhanced tumor treatment

Adrian Domiński[1], Tomasz Konieczny[1], Monika Domińska[2,3], Gabriela Pastuch-Gawołek[2,3], Piotr Kurcok[1]

[1]*Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland*

[2]*Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland*

[3]*Biotechnology Centre, Silesian University of Technology, Gliwice, Poland*

Keywords: supramolecular hydrogel, pH-responsive, Warburg effect, dual drug delivery

The supramolecular hydrogels have gained considerable attention over the last decade in controlled drug delivery systems due to tunable rheological properties and biocompatibility. The supramolecular gels based on the interaction between α-cyclodextrin and poly(ethylene glycol) (PEG) are promising injectable materials. PEG chains can penetrate into the cavities of α-cyclodextrin and form polypseudorotaxanes, which subsequently undergo self-assembly and supramolecular gels are formed. The aim of the present work was to obtain hydrogel formed by a guest-host interaction between α-cyclodextrin and PEG chains derived from micelles made of PEGylated ketal-protected aliphatic polycarbonate copolymer exhibiting pH-sensitivity. The encapsulated in such hydrogel hydrophilic glycoconjugates and the hydrophobic doxorubicin are released in a controlled manner in the acidic environment of tumor tissues.

Acknowledgments: *The work is the result of the research project No. 2015/17/B/ST5/01086 funded by the National Science Centre and by the European Union's Horizon 2020 grant agreement No 872152, project GREEN-MAP.*

5

Atmospheric plasma sprayed ceramic coatings with the ability to catalytic degradation of organic dyes

Alicja Duda[a], Łukasz Hawełek[a], Bartosz Kopyciński[b], Marcin Lis[a], Adriana Wrona[a]

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[b]*Łukasiewicz Research Network, Institute of Engineering of Polymer Materials, Toruń, Polska*

Keywords: atmospheric plasma spraying, ceramics, coatings, dyes degradation

Thermal spray technologies have gained considerable popularity in recent years, mainly due to the very good mechanical and functional properties of the obtained materials. The aim of this study was to fabricate ceramic coatings with photocatalytic abilities by the atmospheric thermal spray APS technology. First, blends of nanometric Al_2O_3 and TiO_2 powders in different mass ratios were prepared and then used as a coating material in the thermal spraying process. The obtained coatings were characterized by the X-ray powder diffraction XRD method. Also, roughness, wettability, and color measurements were carried out. In the last stage of the work, photocatalytic abilities were assessed by analyzing the process of eosin photodegradation. The greatest efficiency of the process was achieved for coatings with 100, 75, and 50% TiO_2 content.

6
Impact of experimental conditions of organic solar cell preparation on photovoltaic response

Paweł Gnida, Paweł Nitschke, Ewa Schab-Balcerzak

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland

Keywords: polymer photovoltaics, polythiophene, bulk heterojunction solar cells

Effect of various factors, such as molar mass, regioregularity of poly(3-hexylthiophene-2,5-diyl) (P3HT) and kind of solvent and concentration used for active layer preparation on photovoltaic parameters of bulk heterojunction solar cells were considered. It was found, that the best efficiencies due to enhanced short-circuit current, were obtained when 1,2-dichlorobenzene was utilized as solvent during spin-coating preparation of active layer. Increase of solution concentration from 10 to 20 mg/mL resulted in more balanced charge carrier transport and consequently higher fill factor. The impact of the molar masses was slightly pronounced, however a positive influence of regioregularity on photovoltaic response was observed.

7
Docetaxel-loaded bioresorbable scaffolds for urooncology

Joanna Jaworska*[a], Mateusz Stojko[a,b], Jakub Włodarczyk[a], Henryk Janeczek[a], Marcin Godzierz[a], Monika Musiał-Kulika, Piotr Bryniarskic, Janusz Kasperczyk[a,b]

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Keywords: docetaxel, poly(lactide-co-glycolide), drug delivery systems, anti-cancer therapy, urooncology

In this study, tubular bioresorbable scaffolds with drug-eluting properties were obtained as a model prostatic stent. Biodegradable layers loaded with docetaxel were obtained on the surface of the scaffolds for local chemotherapeutic delivery. Scaffolds were incubated in artificial urine for 6 weeks and their properties were characterized during this period. Changes in the chain microstructure of the scaffolding polymers were stable. Weight loss of the scaffolds was very low contrary to molecular weight changes. During incubation, slow release of the docetaxel was observed. After 6 weeks, 20% of the drug was released from the coating. The stable release of the cytostatic drug is advantageous.

The docetaxel-loaded prostatic stents obtained with 3D printing and intended for prostatic cancer treatment are novel and would be beneficial before main therapy and also as a post-surgery or post-radiation chemotherapy of prostate cancer (by reducing the possibility of metastasis).

8
Electrosensitive polymeric hydrogels – controlling of the size by applying an appropriate potential

Marcin Karbarz

Faculty of Chemistry, Biological and Chemical Research Center, University of Warsaw, Warsaw, Poland

Keywords: environmentally-sensitive gels, electrosensitivity, volume change transition, microgels, thin gel layers

Among environmentally sensitive "smart" hydrogels that belong to thermo- and pH-sensitive group have been the most intensively studied[1]. However, recently increasing attention has turned to electroresponsive hydrogels. Their unique properties open new possibilities in the construction of novel electrochemical devices: micropumps, microvalves, artificial muscels and advanced drug delivery system. One group of electroresponsive hydrogels consists of those responding to an electric field, which usually contain ionic networks.[2] Hydrogel materials of this kind are usually described in the literature as "electrosensitive". However, there is also another group of electroresponsive gels – namely, ones that undergo a volume phase transition or shape changes in response to a change in the gel oxidation state.[3-7] A redox gel can be formed by introducing a redox active group to the polymer network, making it possible to obtain an electrochemically responsive gel able to significantly change its volume and/or shape by changing the state of oxidation of the redox groups. Preparation, properties, and applications of electrosensitive thin layers and microgels attached to the conductive surfaces will be presented.

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9
Modified mesoporous adsorbents of carbon dioxide

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Keywords: mesoporous silicas, modification, carbon dioxide capture

SBA-15 and MCM-48 mesoporous silicas were modified with functionalized triethoxysilanes by post synthesis method thus indroducing on the pore surface polar N- and P-containing groups. The physicochemical characteristics of the adsorbent samples were studied by nitrogen physisorption, UV-Vis spectroscopy and TG measurements. The adsorption capacity of CO_2 was measured in dynamic CO_2 adsorption regime. Higher capacity for CO_2 adsorption was determined for the modified materials in comparison to the initial ones. Values of 4.2-4.6 mmol/g were achieved for the MCM-48 modified adsorbent. A slight decrease about 5% in CO_2 adsorption capacities was registered for the modified silicas in three adsorption/desorption cycles indicating their high performance stability.

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10
Alginate-based films with essential oils having an antibacterial character

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Keywords: mesoporous silicas, modification, carbon dioxide capture

Components of the natural origin of the final product are in the interest of modern times, so sodium alginate as a polymer base and essential oils as active agents were taken to produce biofilms of antibacterial features in possible use as cosmetic masks and food packing.

Films made of sodium alginate with the addition of sage or/and tea tree essential oils were plasticized with glycerol to improve mechanical properties as pure sodium alginate forms very fragile films. The addition of the essential oils did not influence mechanical properties. However, the films with the essential oils proved antibacterial activity against *Staphylococcus aureus* when the content of these oils was higher, but the films did not reveal activity against *Escherichia coli*.

11
Hybrid nanolayers of star polymers and silver nanoparticles with antibacterial activity

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Keywords: star polymers, polymer nanolayers, silver nanoparticles, antibacterial surfaces, antibacterial activity

The main aim of the studies was to investigate the effect of modification of novel star copolymer nanolayers immobilized on solid supports on the antimicrobial activity of obtained materials. The star copolymers of *N,N'*-dimethylaminoethyl methacrylate and hydroxyl-bearing poly[oligo(ethylene glycol) methacrylate] with hyperbranched poly(arylene oxindole) core were covalently attached to the substrate. The silver nanoparticles (AgNPs) were formed *"in situ"* on the star copolymer nanolayers using only amine groups in the star arms. Antibacterial activity of the star nanolayers loaded with AgNPs was examined.

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12
Biomass-derived itaconic acid-based polyelectrolytes for synthesis of self-assembled nanocomposite hydrogels

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Keywords: free-radical polymerization, bio-based monomers, ionic liquids, hydrogels

We demonstrate how to synthesize the high molecular weight poly(itaconic acid) PIA by using an unusual reaction system, which is an equimolar mixture of itaconic acid and quaternary ammonium salt. The system is hydrogen-bonding stabilized liquid (at r.t) and belongs to so-called Deep Eutectic Monomers group. The high viscosity of such reaction medium strongly affects the kinetics of radical polymerization, accelerating the process and increasing the average degree of polymerization. [Macromol. Rapid Commun. 41, 1900611] The possibility of obtaining PIA with previously unattainable high molecular weights, offers a new perspective on the feasibility of replacing petrochemically derived monomers such as acrylic acid and methacrylic acid by bio-derived itaconic acid. This high molecular weight PIA can be successfully applied to the preparation of organic-inorganic nanocomposite hydrogels. [J. Colloid Interface Sci. 610, 1-12]

13
Phosphorus- and nitrogen-containing triethoxysilanes for surface modification of silica materials

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Keywords: schiff base, aminophosphonate, synthesis, NMR characterisation

Ordered mesoporous silicas are characterized with large pores, tunable pore sizes, high surface area and a large number of highly dispersed hydroxyl groups. The surface silanol groups are key precondition for suitable functionalization with different organic molecules which improve silica network performance as catalysts or adsorbents.

Aminosilicas are one of the most promising adsorbents for capturing CO_2 due to their excellent textural properties and suitable reactive sites. (3-Aminopropyl)triethoxysilane (APTES) is frequently the first choice for functionalization of mesoporous silicates. Based on our experience novel APTES derivatives were reacted with furfural to obtain the corresponding Schiff base in a quantitative yield. Further, the addition of a phosphonate to the Schiff base produced aminophosphonate derivative of APTES. The newly synthesized compounds were structurally characterized and used in the modification of SBA-15 and MCM-48 silica materials.

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14
3D printed hierachic scaffolds based on polysacharides with magneto-responsive capability and cytocompatibility

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Keywords: 4D printing, magnetic particles, magnetic scaffolds, magnetic activity, cytocompatibility

Additive manufacturing is one of the most promising field which is currently developing in regenerative medicine. In this respect, this contribution is focused on the fabrication of the 3D printed scaffolds using fused deposition modeling technique. The scaffolds is consisting of polysaccharide matrix (sodium hyaluronate) and active magnetic filler (carbonyl iron). Such well-printed systems possessing excellent magneto-responsive capabilities and also very good cytocompatiblity. The obtained results shows, that such system is very promissig in the field of 4D printing and tissue engineering.

Acknowledgement: *Authors gratefully thank the project funded by Czech Science Foundation 22-33307S. Authors D.G. and E. K. gratefully acknowledge the project OP RDE Junior Grants of TBU in Zlín, Reg. No. CZ.02.2.69/0.0/0.0/19_073/0016941 for the financial support.*

15
Segmented and aromatic (co)polyimides as membrane materials for CO2 separation

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Keywords: CO_2 selective membrane, segmented copolymers, polyimide, poly(ethylene oxide)

Tackling the problem of global warming involves the control of greenhouse gas emissions to the atmosphere. One of the developing directions of reducing the amount of CO_2 emission is post-combustion carbon dioxide capture using selective polymer membranes. They are characterized by low fabrication and energy costs, simplicity, and an ease of their adaption to installations.

In this work, the combination of segments from two different groups of polymers: glassy (6FDA-4MPD) and elastomeric (PEO) allowed preparation of the new materials with significantly modified gas transport properties, particularly with respect to CO_2/N_2 separation (fivefold increase). The permeability of pure N_2, O_2, and CO_2 through the membranes was measured using the constant volume gas permeation apparatus. The obtained gas transport characteristics of these new materials have been discussed with respect to their morphology studied by means of WAXD, DSC, and AFM techniques.

16
Characterization of PEDOT properties relevant in bioelectronic applications

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Keywords: bioelectronics, neural interfaces, conducting polymers, PEDOT

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most well-researched conducting polymers. Apart from its excellent conductivity and environmental stability, it is also biocompatible, which poses it as a potential candidate in bioelectronics. However, all these characteristics depend strictly on the synthesis conditions. In this work, PEDOT was deposited electrochemically with use of different doping ions. The optimization of each system was caried out with regard to the best electrochemical performance. The surface of the polymers was characterized with use of scanning electron microscopy and Raman spectroscopy, and their biological properties were analyzed *in vitro* using the B35 neuroblastoma cell line.

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17
Enhanced adhesion of PEDOT:PSS by using diazonium salts

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Keywords: diazonium salts, PEDOT:PSS, platinum electrode, adhesion

In my investigations, I am working on the enhancement adhesion of PEDOT:PSS to platinum electrode through an electrochemical reduction of diazonium salts, e.g 4-nitrobenzenediazonium tetrafluoroborate. This kind of electrochemical pretreatment is expected to result in the formation of robust polymer coatings[1] applicable particularly in biomedical engineering brain implants, neural stimulators, cardiac pacemakers.

[1] Villemin, E. et al.; *Synthetic Metals*, **2019**, 248, 45-52.

18
Grafting of gradient polymer brushes under aerobic conditions by SI-*se*ATRP in microliter volumes

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Keywords: SI-ATRP, polymer brushes, microliter volumes

Surface initiated atom transfer radical polymerization (SI-ATRP) is a lively developing technique, which enables synthesis of hybrid materials, characterized by various predefined features. However, traditional approach demands using milliliter volumes of solution as well as maintaining inert atmosphere, which results in high cost of process and difficulties in scaling it up.

In consequence, polymerizations in microliter scale are increasingly presented. Most frequently used approach involves applying reaction mixture directly on modifying material. Herein, the method of simplified electrochemically mediated ATRP in microscale will be introduce. The technique enables polymerization of various monomers in ambient conditions, without deoxygenating the system, leading to hybrid materials decorated with gradient brushes.

19
Dialdehyde chitosan – a non-toxic and effective cross-linking agent for biomedical applications

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Keywords: dialdehyde chitosan, chitosan, polysaccharides, cross-linking

The natural cross-linking agents containing carbonyl groups are of great interest, mainly for modifying the properties of natural polysaccharides. One of the most popular cross-linkers for biomedical applications is glutaraldehyde. However, the unreacted particles can be released from the cross-linked material and cause cytotoxicity. This can be eliminated when using a cross-linker based on polysaccharides. The present study reports the quick and efficient synthesis of dialdehyde chitosan (DACS) and its application to prepare chitosan films. Then, 5, 10, and 15% DACS were used for chemical cross-linking of native chitosan via Schiff base reaction. The obtained materials, forming thin films, were fully characterized in structure and surface morphology. It has been shown that due to better mechanical, thermal, and surface properties as well as lower toxicity of the obtained cross-linked biofilms, dialdehyde chitosan is a very promising cross-linking agent.

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20
Potato starch films plasticized with choline chloride-malic acid deep eutectic solvent

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Keywords: choline chloride, deep eutectic solvent, malic acid, plasticization, starch

For many years starch was tested as a potential replacement for currently used petroleum-based materials. The difficulty with starch processing is that its glass transition temperature is higher than degradation temperature. However, via plasticization, it is possible to lower the value of glass transition temperature. Recently, the growing interest in a new group of plasticizers, i.e. deep eutectic solvents has been observed.

In this work, for starch plasticization, the system based on choline chloride and malic acid was applied (molar ratio 1:1). The starch films were prepared via casting technique. The effect of the plasticizer's components addition method into the starch system has been evaluated. The physicochemical and mechanical properties of obtained films were determined.

21
Novel dimethacrylate copolymers containing quaternary ammonium bioactive groups for dental applications

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Keywords: urethane-dimethacrylates, quaternary ammonium compounds, photocurable dental resins, antibacterial properties, physicochemical properties

Currently used dental composite restorative materials do not have antibacterial properties, which results in significant bacteria gathering on their surfaces. It causes tooth decay and inflammations of surrounding tissues. In this study, a series of novel urethane-dimethacrylate monomers containing quaternary ammonium groups (QAUDMA) were formulated with triethylene glycol dimethacrylate (TEGDMA) to achieve polymers, which might serve as potential matrices in dental composites. These polymers showed intense antibacterial activity against *S. mutans* and *E.coli*, low polymerization shrinkage, satisfactorily high glass transition temperature, and degree of conversion. Water sorption was higher compared to the standard Bis-GMA/TEGDMA dental copolymer, which can be explained by the presence of quaternary ammonium groups.

22
Synthesis and characterization of amphiphilic polyglycidol-polystyrene-polyglycidol (ABA) block copolymers

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Keywords: polystyrene, polyglycidol, amphiphilic block copolymer, diphenylethylene

1,1-Diphenylethylene (DPE) was widely used for anionic polymerizations to obtain a vinyl (co)polymers with well controlled structures. The unique property of DPE is an ability to react with alkali metals leading to formation of a DPE-dimer with two active carbanion species. DPE-dimer can be simply used for syntheses of various ABA type copolymers. The aim of the studies was preparation and characterization of amphiphilic tri-block copolymers containing polystyrene central block and polyglycidol flanking segments. Modification of DPE based chemistry makes possible to get series of amphiphilic polyglycidol-polystyrene-polyglycidol tri-block copolymers. The polymerization degree (DP_n) of polystyrene block was identical for all synthesized copolymers (DP_n = 60), whereas (DP_n) of polyglycidol was in the range 11-63. The dependence of water wetting angles on the surfaces of synthesized copolymers films was investigated.

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23
Ring opening polymerization of rac-lactide and ε-caprolactone promoted by titanium complexes of ONO and ONN-type Schiff base ligands

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Keywords: rac-lactide, ε‑caprolactone, titanium complex, ring opening polymerization

A series of new titanium complexes supported by phenoxy-imine ligands with pendant N- or O-donor group were synthesized and characterized. All complexes were used as catalysts in ring opening polymerization of *rac*-lactide and ε‑caprolactone. The influence of complex structure as well as reaction parameters (monomer/transition metal molar ratio, reaction time, polymerization temperature) on monomer conversion and product properties were investigated.

24
MALDI mass spectrometry monitoring of cyclodextrin-oligolactide synthesis

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Keywords: MALDI MS, cyclodextrin, oligolactide, ring-opening oligomerization, MS/MS fragmentations

Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI MS) represents a powerful analytical technique for monitoring the minute changes of the molecular weight and characterizing complex chemical structures. Therefore, the ring opening reaction of D,L-lactide in the presence of β-cyclodextrin was performed in different solvents (N,N-dimethylformamide, N-methylpyrrolidone, and dimethyl sulfoxide) and temperatures to establish their influence on cyclodextrin-oligolactide (CDLA) synthesis. The evolution of molecular weights obtained by MALDI MS was also confirmed by ^{1}H NMR spectroscopy with an excellent agreement between the two techniques. In CDLA synthesis, transesterifications are the main side reactions, but they are not the only ones as different solvents may interfere with the ring-opening process leading to structural changes of the main product. Therefore, the MS/MS fragmentation studies were employed to gain further insights into the structure of CDLA products.

25
Synthesis and characterization of DDMAT as chain transfer agent for *e*RAFT polymerization

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Keywords: RAFT, radical polymerization, trithiocarbonates, CTA, DDMAT

The right selection of a suitable chain transfer agent (CTA) is crucial for the course of RAFT polymerization processes. Properties of these compounds determine the feasibility of the polymerizations, as well as the characteristics and features of the received polymer materials. In the case of electrochemical mediated reversible addition-fragmentation chain-transfer polymerization (*e*RAFT) in addition to the chemical properties, the appropriate electrochemical characteristics of CTAs are becoming the key to the success. In this work, the synthesis, characterization (i.e. spectroscopic and electrochemical specifications), and also application in RAFT processes as CTA early results of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DDMAT) were presented. The use of DDMAT in *e*RAFT polymerizations, which in the prospective aim of the work, was briefly considered as well.

26
Synthesis of modified poly(β-butyrolactone) by block copolymerization with oxiranes

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Keywords: block copolymers, biodegradable polymers, anionic polymerization, oxiranes

The aim of presented work is the tune properties – philicity and biodegradation rate of poly(β-butyrolactone) by controlled block copolymerization with hydrophilic oxiranes (glycidol and ethylene glycol).

Block Copolymers with AC, ABC, symmetrical CAC and also CBABC block arrangement were synthesized via anionic ring opening polymerization using sequential monomer addition technique and PEG macroinitiator. The respective blocks are A – poly(ethylene glycol), B – polyglycidol, C – poly(β-butyrolactone). An important aspect of presented work was the development of a method of quantitative conversion of alcoholate growth centres of living polyoxirane chains, characteristic for cyclic ethers polymerization, to carboxylate growth centres, essential for the initiation and controlled polymerization of β-butyrolactone.

27
Influence of the plasticized-PVC specimen preparation methods for testing of plasticization efficiency on the determined final product crucial properties

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Keywords: plasticizer, PVC, solution casting, extrusion, plasticizing efficiency

Nowadays research efforts focus on the designing of new plasticizers that might replace hazardous phthalate in PVC processing. To assess the plasticizing efficiency two methods of samples preparation were compared: (1) traditional method – usually used in industry, and (2) solution casting method – commonly used in RD and academia for new plasticizers examination. To compare the plasticization efficiency of plasticized PVC between both specimen preparation method set of measurements were conducted: elongation at break and tensile strength (mechanical properties); exudation and leaching in n-hexane (migration resistance); and thermal stability and glass transition temperature. The result of the study clearly shows that the solution casting method used commonly in RD facilities does not fully reflect the condition industrial scale plasticization of PVC and thus, can be applied only for a preliminary assessment of the effectiveness and suitability of a newly synthesized plasticizer.

28
Synthesis and characterization of amphiphilic polymer networks

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Keywords: telechelic macromonomers, amphiphilic polymer networks, injectable biomaterials, adhesive surfaces, tissue engineering

Advanced biomaterials have become a powerful tool to enhance the diversity of applicability of various inorganic/organic, hydrophobic/hydrophilic and elastic/stiff materials in medical field. Added value can be their injectability or controlled porosity making them suitable for tissue engineering applications. Moreover, elastomeric properties and bioadhesiveness can make them suitable for soft tissue repair. Herein, we present the synthesis of amphiphilic polymer networks consisting fatty acid derived ester-urethane telechelic macromonomer being used in combination with PEGylated fibrinogen to create amphiphilic polymer networks. In order to induce adhesion to wet surfaces, a mussel adhesive protein was used in final formulations. The *in vitro* cytocompatibility and adhesive properties assessment studied by fluorescent microscopy and peeling test indicated lack of cytotoxicity and good adhesion to wet surfaces.

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29
Polymeric zinc diorganophosphates as latent catalysts in epoxide polymerization

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Keywords: hybrid polymer, epoxide polymerization, latent catalyst, epoxy resin curing

Zinc diorganophosphates (ZnDOPs) are hybrid 1D polymers with a general formula of $Zn[O_2P(OR)_2]_2$, whose basic structural units are linear chains formed by ZnO_4 tetrahedra connected by the bidentate $O_2P(OR)_2$ ligands. The parallel location of the $Zn[O_2P(OR)_2]_2$ chains favor the formation of crystalline domains. The intermolecular interactions between neighboring chains in such domains can be changed by temperature leading to reversible structural transformations and some new properties of ZnDOPs (*e.g.*, catalytic activity).

In this communication we will present the results of XRD and DSC analyses, rheological tests, as well as NMR and MALDI-ToF experiments concerning the use of ZnDOPs as catalysts for a high temperature polymerization of ethylene oxide and curing of Bisphenol A diglycidyl ether.

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30
PDMAEMA/polyester miktopolymers: synthesis, physicochem-ical characterization and hydrolytic degradation

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Keywords: semi-degradable polymers, miktopolymers, hydrolytic degradation, PDMAEMA

Miktoarm polymers are of special importance because they comprise the unique properties of totally different species. The aim of our study was to synthesize well-defined semi-degradable A_5B type miktopolymers: $[PDMAEMA]_5[PCL]$, $[PDMAEMA]_5[PLA]$, $[PDMAEMA]_5[PLGA]$, $[PDMAEMA]_5[PLGCL]$. The next step was physicochemical characterization and investigation of hydrolytic degradation of the obtained miktostars. The progress of the degradation was moni-tored by size exclusion chromatography and nuclear magnetic resonance spectroscopy. The results showed that the obtained polymers are good candidates for long- or mid-term period drug-delivery systems.

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31
Thermal stability, viscoelastic and mechanical properties of polyurethanes obtained with the use of bio-monomers

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Keywords: bio-polyurethanes, mechanical properties, thermal stability, viscoelastic properties

This work involves polyurethanes (PUs) and their thermal stability, viscoelastic and mechanical properties. The properties of this group of polymers strongly depend on substrates used for their synthesis, monomers' molar ratio, or processing methods. Polyurethanes were synthesized with the use of two types of bio-monomers (bio-based polyester polyols and bio-glycols) and petrochemical diisocyanate (hexamethylene diisocyanate). PUs materials were synthesized at three NCO/OH molar ratios: 0.9, 0.95, and 1.0. It was confirmed that the type of polyester polyol, bio-glycols, and the isocyanate index played a key role in the mechanical and viscoelastic properties. Despite the bio-monomer type, the thermal degradation occurred in two main steps.

32
PAC (pharmaceutical active compounds) influence on the course of the polypyrrole synthesis

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Keywords: polypyrrole, salicylate, immobilization, impedance analysis

In our work, we present the results of electrochemical analysis of polypyrrole deposited on the surface of a steel electrode in the presences of chosen PAC (pharmaceutical active compounds) namely salicylic acid and sodium salicylate. The impedance characteristic of the SS316 L coating with pPy samples were proposed along with morphology studies. The mutual dependence of the synthesis condition and electric properties were traced.

33
The synthesis of polyester precursors for the synthesis of polyurethanes via oxidative esterification of aliphatic α,ω-diols

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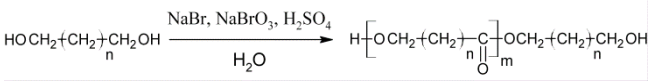
Polyester polyols commonly used for the synthesis of polyurethanes, in particular coating materials and rigid foams, account for about 25% of all polyols produced[1]. Their use in polyurethanes has a positive effect, among others, on tensile strength, abrasion resistance, UV radiation and the action of oils. In addition, it provides the resulting formulations with low temperature flexibility and thermal stability.

Polyester polyols are commonly synthesized via polycondensation reaction of diols with diacids or their diesters. Herein, we demonstrate an alternative route to polyester polyols via oxidative esterification of aliphatic α,ω-diols. Unlike polycondensation reaction, the process is carried out in aqueous media at 30°C and atmospheric pressure[2]. In situ generated hypobromous acid from the mixture of NaBr, $NaBrO_3$ and H_2SO_4 was used to trigger the reaction[3]. The reaction progress can be conveniently controlled with Br/OH molar ratio. The properties of obtained polyesters are determined by the applied diol and can be tailored by using a mixture of diols. The composition of polymers was determined with GPC, NMR, and MALDI TOF MS. It is shown that polyesters obtained with this method can be used as precursors for polyurethanes synthesis. This work provides a quick and convenient route to polyester polyols synthesis, feasible for any laboratory.



Scheme 1. Synthesis of polyester polyols from aliphatic **α,ω**-diols in an oxidative process

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34
Polylactide containing tetraphenylethane groups as a new approach to PLA copolymers

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Keywords: polylactide copolymers, iniferter, tetraphenylethane

One of the ways of bio-derived polylactide modification is copolymerization with other monomers. The aim of this study was to obtain polylactide block copolymers with vinyl monomers using "iniferter" concept. Tetraphenylethane (TPE) unit undergoes thermal dissociation creating free radicals, which are able to initiate a radical polymerization.

To introduce TPE group into PLA chain and initiate vinyl monomer polymerization in the next step, we developed several approaches. These methods are based on using 4-hydroxybenzophenone (HBP) as a starting point, and its functionalization leading to the attachment of primary -OH groups. In the first approach, HBP-EtOH was used as an initiator of LA polymerization, obtained polymer was then coupled under UV radiation resulting in PLA chain with one TPE unit. In the second approach, HBP-EtOH was first coupled (UV) to give TPE derivative and then introduced to PLA chain by coupling with PLA diols using diisocyanate. Obtained PLA-based polymers with one or multiple TPE units were used as „macroiniferter" in the polymerization of acrylonitrile under moderate heating.

35
Composition, hydrogen bonding and viscoelastic properties correlation for ethylene/*α,ω*-alkenol copolymers

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Keywords: ethylene, *α,ω*-alkenol, copolymers, hydrogen bond, viscoelasticy

Copolymers of ethylene with polar comonomers exhibit a number of beneficial properties compared to ethylene/1-olefin copolymers [1]. In literature data there is no information related to the influence of composition of ethylene/*α,ω*-alkenols copolymers on the macromolecular and viscoelastic properties. In the present work, the SSA, FT-IR and Shear Rheometry methods were applied to characterize ethylene/10-undecen-1-ol and ethylene/9-decen-1-ol copolymers with different comonomer content. The main objective of the work was to understand how polar comonomer content and its distribution along polymer chains and *α,ω*-alkenol structure, influence the rheological behavior of these copolymers.

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36
N-sulfopropylation of chitosan under neutral conditions with a controlled degree of substitution

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Keywords: N-(3-sulfopropyl)chitosan salt, polyampholyte, 1,3-propane sultone, degree of substitution, quantum chemistry calculations

A conjugation of sulfonate groups to chitosan (CS) converts the CS containing ionizable cationic groups to its polyampholyte derivatives, which are used in applications benefiting from both ionizable cationic and anionic groups. The subject of this work is to study *N*-sulfopropylation of CS with 1,3-propane sultone (PrS) under aqueous conditions toward the synthesis of *N*-(3-sulfopropyl)chitosan salt (SPCS), a CS polyampholyte. According to the literature, this reaction in acidic conditions should lead to SPCS of a high degree of substitution (DS). We found that such information is ambiguous because it does not take into account the massive PrS hydrolysis leading to the amine-sulfopropyl salt formation. This salt contaminates SPCS by electrostatically driven complexation with amine groups of CS and provides artificially high DS. We overcame this shortcoming by synthesizing SPCS under neutral conditions that affords a proper control over DS up to 95%. We established that true DS for SPCS can be obtained by NMR. The underlying mechanisms involved in SPCS synthesis are identified with the assistance of quantum chemistry calculations.

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37
Synthesis of polyester networks based on Tulipaline A

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Keywords: polyester, tulipalin A, covalent adaptable networks (CANs), self-healing

Copolymers of ε-caprolactone (ε-CL) and α-methylene-γ-butyrolactone (MBL) [P(MBL-co-CL)] with different molecular weight and MBL content were obtained, either Linear P(MBL-co-CL) using different coordination-insertion catalysts [1, 2], or multiarm P(MBL-co-CL) by using a catalyst/initiator system for the cationic ring-opening copolymerization according to the activated-monomer mechanism were obtained [1].

The crosslinking of the obtained P(MBL-co-CL) with different dithiols and diamines will be optimized. The thermal properties such as Tg and Tv will be estimated. In addition, the different mechanical properties, such as stress relaxation modulus, energy storage and loss modulus tensile strength, young's modulus will be determined.

Finally, the self-healing, reprocessability and recyclability ability of the obtained polyester networks will be evaluated.

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38
Synthesis of novel organofunctional polyolefins

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Keywords: post-polymerization, homogeneous catalysis, organosilicon, functional polymer

Nowadays, over 150 million tons of polyolefins are produced annually worldwide. The common organic polyolefins (PE, PP) exhibit poor compatibility to nitrogen- or oxygen-containing compounds, polar pigments and low adhesion to inorganic surfaces. Thus, the introduction of functional groups into polymer chains is highly desirable since it would increase the number of potential applications and render these materials even more versatile. In this contribution, an efficient methodology for the synthesis of new organofunctional polyolefins is proposed. It includes the synthesis of new polymeric precursors and their subsequent functionalization through transition metal-catalyzed reactions. The developed synthetic strategies enable the incorporation of a wide variety of organic and groups into the polymer chains, which cannot be introduced through conventional polymerization protocols. This research was supported by National Science Centre, Poland, UMO-2019/32/C/ST4/00178.

39
Unsaturated nucleophiles as efficient initiators for nitroalkenes polmersation process

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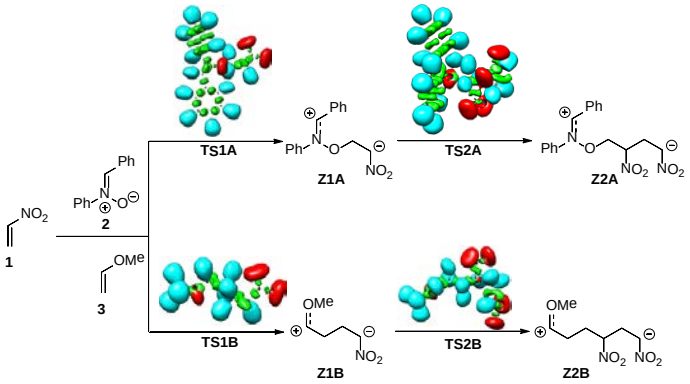
Keywords: nitroalkenes, polymerization process, DFT study, molecular electron density theory

The DFT computational study shed light on the kinetic aspects as well as the molecular mechanism of zwitterionic polymerisation of simple conjugated nitroalkenes. These reaction can proceed under relatively mild conditions. The exploration of reaction profiles show, that the first reaction stage exhibit evidently polar nature, whereas, additions of further CNA molecules to the polynitroalkyl molecular system formed, should be considered as moderatate polar processes. In BET analysis of the bonding changed along the analyzed key stages of the polymerization reaction between nitroethene and (Z)-C,N-diphenylnitrone, we can distinguish eleven topologically different phases. While the first step of these polymerizations are associated with the rupture of the double bond in nitroethene molecule and formation of pseudoradical center, the second step are associated with formation of single and double bonds.



40
Synthesis of lactide/cyclic acetals copolymers

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Keywords: copolymers, cyclic acetals, functionalization of polylactide, ring-opening polymerization

Polylactide is deemed a versatile polymer with a high application potential due to its biocompatibility. The degradability of this polyester is a crucial feature not only for biomedical applications but also in the context of the growing environmental pollution. It is possible to modulate the properties of polylactide by copolymerization with properly selected monomers. Presented work aimed to introduce into the polylactide chain comonomer that can affect the rate of polymer degradation. To obtain polyesters containing units that are more sensitive for hydrolysis than esters bonds the cationic copolymerization of lactide with various cyclic acetals was applied. We have investigated the cationic copolymerization of lactide with three differently functionalized or nonfunctionalized cyclic acetals: 4-chloromethyl-1,3-dioxolane (ClDXL), 4-[(allyloxy)metyhl]-1,3-dioxolane (AllylDXL) and dioxepane (DXP). The structure, molecular weight, and dispersity were carefully analyzed by using ^{1}H NMR ^{13}C NMR, 2D NMR, and SEC.

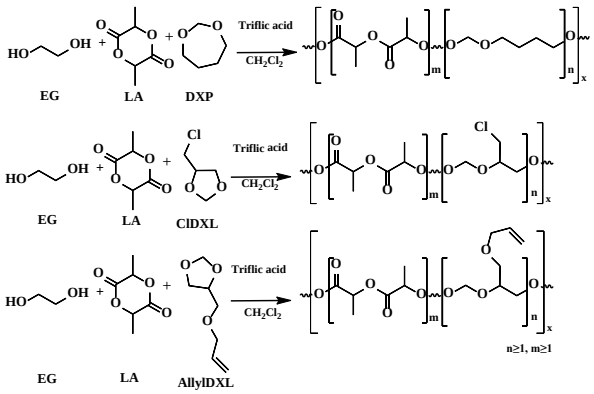

Figure 1. The synthesis and the structure of polylactides containing different acetal units

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41
Impact of size and shape of stimuli-responsive polymers onto inor-ganic crystals growth mechanism

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Keywords: polyacid, KCl, crystallization, phase transition

The aim of these studies was to investigate the impact of the composition and topology of stimuli-responsive polymers onto KCl crystallization. Linear poly(acrylic acid) (PAA) and star-shaped poly(acrylic acid-*co*-methyl acrylate) (PAA-*co*-MA) were used for isohydric crystallization by cooling of KCl in a deionized water solution. The results showed that the polymer's phase transition had an important role in the crystallization process. It did not impact the nucleation temperature. However, depending on the properties of polymers different growth mechanisms were observed leading to the creation of different crystal structures, e.g. hollow cuboids.

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42
Thermal analysis of new amino-functional β-cyclodextrin oligomers

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β-cyclodextrins (β-CD), in terms of release and absorption, are a promising object for research. β- CD was functionalized with an amino group, then an oligomer was formed therefrom using a polycondensation reaction with a dianhydride. The ability of β-CD oligomers to form chitosan hydrogels was used in this project. First attempts were made to create stable spheres that would absorb boron compounds from the solution. For the correct characterization of the intermediates, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) analysis were performed. A general overview of the oligomers was obtained. An accurate assessment of the weight loss of the samples was obtained, considering the first loss as water evaporation and the next as decay. DSC analysis gave information on the intensity of thermal effects of the decomposition of the samples.

43
Metal organophosphates as new nucleating agents for isotactic polypropylene

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Keywords: polypropylene, nucleation, organophosphates

The paper presents studies of the influence of metal organophosphates differing in the type of metal (Ca, Zn, Al) and containing various organic substituents (methyl, ethyl, phenyl) as nucleating agents of isotactic polypropylene. The effect of the type and content of organophosphates on the crystallization behavior of iPP was investigated by DSC and WAXS methods. A significant increase in the temperature of the peak crystallization was found; in the case of PP/1% ZnMPhP even by 13.2^{o}C, and an increase in the degree of crystallinity as compared to the original polymer. Moreover, the half-time of non-isothermal crystallization was shortened; e.g. for PP/1% AlDEP by as much as 43% compared to polypropylene without any additives. WAXS measurements showed that the incorporation of calcium organophosphates into isotactic polypropylene resulted in an increase in the β-phase content, while other organophosphates favoured crystallization of iPP in a monoclinic system.

44
Bioplasticizers based on succinic acid for poly(vinyl chloride)

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Keywords: bioplasticizers, poly(vinyl chloride), succinic acid, oleic acid, esters

Plasticizers are widely used as additives in the polymer industry to improve the properties and processing characteristics of polymers. About 90% of the world's plasticizer production (mainly phthalate plasticizers) is used to produce flexible polyvinyl chloride (PVC). Unfortunately they easily migrate from the polymer matrix, thus posing a threat to human health and the environment. In our research, a procedure for obtaining a bioplasticizer from environmentally friendly renewable raw materials was developed. Epoxidized esters were synthesized in three steps from propylene glycol, oleic acid and succinic acid. The obtained bioplasticizer is a mixture of monoesters and diesters containing an oxirane group in their structure. Plasticizer is characterized by greater resistance to migration compared to phthalate plasticizers available on the market (i.e. DEHP), while maintaining very good strength properties of the molding.

45
Functional group modification of polyamidoamines

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Keywords: polyaddition, ring-closing, dehydration catalysts, lactams

A wide range of functional polymers can be synthesized from α-methylene-γ-butyrolactone (MBL) using various polymerization techniques such as free radical polymerization, reversible-deactivation radical polymerization, anionic or cationic polymerization, ring-opening polymerization, etc. [1-3], which can help to replace various petroleum-based polymers with natural sources. The polyaddition of MBL using diamines replaces the oxygen with nitrogen, opening possibilities of producing polyamidoamines.

In the present work, polyamidoamines with a pendant hydroxyl group is subjected to a dehydration catalyst, $ZnCl_2$ in a solvent mixture of acetic acid and water, to remove the pendant hydroxyl group and make the amide units in the main-chain into lactam units. The preliminary results were confirmed by NMR and IR analysis, with further support from the TGA and DSC studies. Various other experiments are needed to be done to study the effect of acid concentration, temperature, and reaction medium on the ring-closing mechanisms.

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46
Positron annihilation lifetime spectroscopic analysis of plastic deformation of polypropylene

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Keywords: polypropylene, plastic deformation, PALS, cavitation phenomenon

The positron annihilation lifetime spectroscopy (PALS) was used to track the deformation-induced changes of the structure of the amorphous and crystalline component of polypropylene. The studies, after appropriate adaptation of the PALS technique in accordance with the methodology presented in the previous work [1], were carried out in the range of local strains (LS) 0-0.20, wherein the yield point was observed at LS=0.10-0.13. Based on the results of the mean o-positronium lifetime (τ_3) in a function of local strain, it was indicated that the average size of the free volume pores of the amorphous phase in the studied strain range decreased in comparison with the undeformed polypropylene. The observed deformation-induced evolution of the pores dimension had a gradual character/nature, proportional to the observed changes of the thickness of the amorphous layers. It was also shown that the cavitation phenomenon was responsible for the increase of the dispersion of o-positronium lifetime (σ_3).

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47
Enzymatic esterification of itaconic acid

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Keywords: itaconic acid, itaconic esters, renewable monomers, enzymatic esterification, lipase

Itaconic acid is a vinyl monomer obtained biotechnologically on an industrial scale. It is a non-toxic, renewable biomaterial that can be used in polymerization processes as a replacement for non-renewable monomers, such as acrylic and methacrylic acid [1,2].

The purpose of this study is to obtain esters of itaconic acid in enzymatic esterification reactions, which might become new monomers from renewable raw materials. Itaconic acid esterification and dimethyl itaconate transesterification were performed using lipase enzyme as a biocatalyst [3]. Alcohols of various structures were used in the research in order to obtain diverse derivatives of itaconic acid. The reactions were performed in organic solvents and the structure of the compounds obtained was analyzed by the GC-MS as well as $_1$H, $_{13}$C and 2D NMR.

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48
Thermoresponsive cholesterol-terminated copolymers for doxorubicin delivery

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Keywords: cholesterol, poly(*N*-isopropylacrylamide), drug delivery system, thermoresponsive polymers, RAFT/MADIX

Cholesterol is a key building block of mammalian cell membranes, which is responsible for fluidity, integration, and permeability.[1,2] It is a common choice as a guiding and membrane penetrating molecule in Smart Drug Delivery Systems (SDDS).[3] One of the most popular release approaches is to use thermosensitive blocks such as poly(*N*-isopropylacrylamide) (PNIPAAm).[4] β-Diketones are well-known chelating agents that form stable complexes with various metal ions. Due to its structure, acetylacetone derivative (AcacI) is able to create hydrogen bonds with hydroxyl groups of drug molecules. Copolymers were obtained by reversible addition-fragmentation chain-transfer (RAFT) polymerization. Physicochemical and biological properties of drug carriers and its conjugates with doxorubicin will be presented.

Acknowledgments: *NCN, grant OPUS nr 2016/21/B/ST5/01365, analyses were performed in the Centre of Synthesis and Analyses BioNanoTechno of the University of Bialystok.*

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49
Synthesis and characteristic of “green” polyurethane foams obtained from chosen bio-based monomers

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Keywords: polyurethane foams, prepolymer, bio-based polyol, bio-based diisocyanate

The aim of this study was to synthesize polyurethane foams (PUR) (with increased “green” carbon content to conventional PUR) using different types of bio-derived monomers. For this research, both one-step and two-step methods were used[1]. At the first stage the aliphatic isocyanate Tolonate X FLO 100 (with 32% of "green" carbon content) was reacted with VelvetolH2400 (PO3G) ether bio-polyol (with 100% of "green" carbon content) to obtain bio-based prepolymers terminated with isocyanate groups. In the next step, mixtures consisting of polyol, and/or glycol, water, catalyst and surfactant were prepared. The synthesized earlier ether-urethane bio-based prepolymer was added to the prepared mixtures. The polyurethane systems were mixed mechanically. Also foams with previously prepared polyol mixture and petrochemical diisocyanate or/and diisocyanate mixture were obtained for comparison purposes of different foam materials. The obtained polyurethane materials were then characterized for chemical structure, thermal stability and mechanical properties.

An increase in the elasticity of the materials obtained using bio-based isocyanate was observed during the tests. The thermal stability of the materials containing the residues of glycol or bio-based isocyanate was lower than that of the materials prepared with petrochemical diisocyanate pMDI or without glycol.

The analysis showed a significant influence of the substances of natural origin on the structure and properties of polyurethane materials. This is mainly due to their complex structure. It was proved that it is possible to obtain foamed materials with the use of bio-components. Their properties can be modified by adjusting the ratios of the used reactants. The obtained foam materials can be successfully put to various applications.

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50
Vanadium catalysts with oxazoline ligands for ethylene-norbornene copolymerization

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Keywords: vanadium catalyst, oxazoline, ethylene, norbornene, copolymer

Cyclic olefin copolymers (COCs) are a promising group of materials with specific, projectable properties that can be controlled by the design of catalysts. The choice of transition metal and ligands, especially N-donor ligands, play a key role in the performance of COCs coordination copolymerization. A series of complexes with vanadium metal center and ligands having 1,3-oxazoline as main structural molecular fragment substituted by pyridine, phenol, or 1,3-oxazole were synthesized, and after activation by $AlEt_2Cl$, were tested as catalysts in ethylene-norbornene copolymerization. It has been shown that the vanadium catalysts with oxazoline ligands are suitable for the copolymerization. The type of ligand influences the course of polyreaction and the physical properties of the polymers obtained.

51
Structure and mechanical properties of high-density polyethylene composites with glassy carbon

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Keywords: high-density polyethylene (HDPE), polymer composites, glassy carbon (GC), X-Ray diffraction (XRD), residual stress analysis (RSA)

We investigated an impact of glassy carbon (GC) reinforcement at crystal structure and mechanical performance of high-density polyethylene (HDPE). In our research, we compared HDPE/GC composites with HDPE filled with carbon nanotubes (CNT), graphene (GNP) and graphite (Gr). We made composite samples by mixing HDPE granules with respective powders in ethanol followed with melt mixing at laboratory extruder. To evaluate crystal structure and crystallinity, we used X-ray diffraction (XRD) and differential scanning calorimetry (DSC). We supported XRD results with a residual stress analysis (RSA) according to EN15305 standard. Analysis showed that reinforcing with GC leads to significant crystallite size reduction and low residual stress values. We evaluated mechanical properties of composites with hardness and tensile testing. Addition of glassy carbon results with increase mechanical strength similar to composites with CNT and GNP.

52
Control of the ability to crystallize of 2-isopropyl-2-oxazoline-based copolymers

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Keywords: poly(2-oxazoline)s, 2-oxazoline copolymers, ability to crystallize, modifications of polymers

Poly(2-isopropyl-2-oxazoline) exhibits a phase transition in aqueous solution at so-called physiological temperature, which, combined with its low cytotoxicity, makes this polymer potentially interesting for bioapplications. On the other hand, this homopolymer is also prone to crystallize, what seems to be detrimental for some uses. In this work, series of 2-isopropyl-2-oxazoline (iPrOx) -based copolymers, with 2-n-propyl-2-oxazoline, 2-methyl-2-oxazoline, 2-ethyl-4-methyl-2-oxazoline, 2-(3-butenyl)-2-oxazoline and ethyleneimine were obtained and they were characterized in terms of thermal and crystalline properties, both in the solid state and in solutions. It is verified, if the structure-property relationship of the copolymers could be varied in a controlled manner, and if it is possible to obtain amorphous iPrOx-based copolymers.

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53
Algal and yeast waste fraction valorisation for the biosynthesis of poly(γ-glutamic acid), a versatile biomaterial

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Keywords: industrial biotechnology, biomaterials, circular economy, drug delivery systems, biopharmaceutical

Valorisation of different types of waste streams can encourage widespread industrial focus towards cost-competitive sustainable biomaterial development. Herein we demonstrate the use of complementary organic waste fractions for the biosynthesis of poly(γ-glutamic acid) (γ-PGA), a versatile microbiolgicaly derived biopolymer.

The biosynthesis of this biomaterial is achieved through re-utilisation of post-extracted algal biomass and post brewery yeast fractions in a sustainable and cost-effectve manner.

Physico-chemical characterisation of the produced polymeric material suggests suitability for use as UV protectant, cryoprotectant, drug delivery system and bioremediation agent.

54
Bio-based polyester polyols for green polyurethane materials

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Keywords: bio-based polyester polyols, green polyurethane foams, chemical structure, mechanical properties, thermal stability

The synthesis of polyols from renewable substances as an alternative for petrochemical-based polyols play important matter in the polyurethane industry. The polyester polyols with 100 % bio-carbon content were synthesized with the use of succinic acid (bio-SA), azelaic acid (AAz) and 1,3-propanediol (bio-PDO), all with natural origin. The syntheses were conducted via polycondensation reaction to obtain products with planned chemical structure, average molecular weight and functionality, which indicate their application in polyurethane materials. The results indicate that the novel polyester polyols revealed similar properties to the commercially used petrochemical-based counterpart. Bio-based polyurethane materials were also synthesized and selected properties were measured.

55
Cyclodextrin-oligocaprolactone synthesis – advanced structural studies by MALDI mass spectrometry and NMR spectroscopy

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Keywords: cyclodextrin, ε-caprolactone, MALDI MS, NMR spectroscopy, tandem MS

Cyclodextrins were previously proved to be active in catalysis of cyclic esters ring-opening reactions, hypothetically, in a similar way as lipase-catalyzed reactions. However, the way they act remains unclear. Herein, we focus on the synthesis and characterization of β-cyclodextrin-oligocaprolactone (CDCL) products obtained via ring-opening of ε-caprolactone in the presence of organocatalysts such as 4-dimethylaminopyridine and (–)-sparteine, or pure solvents. Bulk or supercritical carbon dioxide polymerizations led to inhomogeneous products. Our approach consists of solution polymerization, in dimethyl sulfoxide and dimethylformamide, respectively, to obtain homogeneous cyclodextrin derivatives. MALDI mass spectrometry and NMR techniques were used to establish the substitution degrees and patterns for the obtained CDCL derivatives. Also, the mass spectrometry evaluation was further enhanced by fragmentation studies which confirmed the attachment of oligoesters to the cyclodextrin.

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56
CALB-mediated enzymatic synthesis of poly(glycerol sebacate) prepolymer: investing a synthesis of a novel prepolymer for tissue engineering

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Keywords: poly(glycerol sebacate), enzymatic synthesis, biomedical polyesters, tissue engineering

Poly(glycerol sebacate) (PGS) is a novel elastomeric polyester indicated for tissue engineering application. For the aforementioned function, the polymer is commonly subjected for cross-linking. This process is affected by the prepolymer structural properties resulting from the synthetic pathway. The presented study regards the optimization of an enzymatic synthesis of PGS prepolymer (pPGS), conducted in various temperatures, in 1,4-dioxane (DX) using *Candida Antarctica* Lipase B (CALB) as a catalyst. Enzymatic synthesis is perceived as a more controlled process than conventional polycondensation. Therefore, in order to obtain polymer with desired properties such as molecular mass or branching degree – the process requires to be investigated. The reactions were performed using sebacic acid and glycerol as well as dimethyl sebacate (DMS) and GLY as initial monomers.

57
The influence of polyethylene microstructure on mechanical properties of its amorphous regions

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Keywords: interlamellar amorphous phase, semicrystalline polymers, elastic modulus

A universal method of determining the elastic modulus of the interlamellar amorphous phase of semicrystalline polymers was described in our recent work on the example of high density polyethylene (HDPE) [1]. The swelling-induced local strain (ε_a) and local stress (σ_a) of the interlamellar amorphous regions were estimated basing on the changes of the long period (*LP*) and the yield stress, respectively. Further research was carried out on relation of elastic modulus of the interlamellar amorphous phase and polyethylene microstructure. Three different polymers: HDPE, LDPE (low density polyethylene) and EOC (ethylene – octene copolymer) with different thickness of the lamellar crystals were analyzed. The change of the elastic modulus of the interlamellar amorphous phase with the crystal thickness had linear character. Such relation was justified as a result of decreasing "activity" of α relaxation processes of the crystalline component with the increase of the crystal thickness.

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58
Direct synthesis of oligo-[(R)-3-hydroalkanoates]

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Keywords: poly-[(R)-3-hydroxyalkanoate], oligo-[(R)-3-hydroxyalkanoate], thermal degradation, PHA

Oligo-[(R)-3-hydroalkanoates] (OHA) are biobased and biodegradable oligomers that can serve as building blocks in polymer synthesis and can find use in areas such as medicine, material science or cosmetics. However, the oligomers are usually prepared via multi-step and time-consuming methods with limited scalability that restricts their wider use. More direct methods for preparing OHA from bacterial poly-[(R) -3-hydroxyalkanoate] (PHA) using alkaline agents have been investigated. Preparation by alkaline degradation of the polymer in aqueous solution was successful, but very time consuming. Preparation by thermal degradation of the polymer proved to be more effective. It was possible to advantageously use technical-grade PHA, which contained a pro-degradative impurities, or directly bacterial biomass treated with a catalytic amount of hydroxide.

59
Poly(oligoethylene glycol methacrylate) star-shaped copolymers with hydroxypropyl methacrylate cores

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Keywords: poly(hydroxyl propyl methacrylate), star copolymers, RAFT, light scattering, cryo-TEM

The synthesis of star-shaped copolymers with crosslinked cores and different number and length of arms prepared by RAFT polymerization technique is reported. Hydroxypropyl methacrylate (HPMA) was utilized for the formation of the crosslinked core, with the use of ethylene glycol dimethacrylate (EGDM), a bifunctional monomer in the role of the crosslinker. Oligoethylene glycol methacrylate ($OEGMA_{500}$) was utilized as a biocompatible and hydrophilic component for the creation and extension of the arms. Thus, four star-shaped copolymers were synthesized with different core crosslinking densities, influencing the number of star arms. DLS studies of copolymers in DMF solutions provides sizes of individual copolymer molecules in the range of 8-20 nm. Aqueous dispersions of copolymers studied by DLS and cryo-TEM show formation of spherical star-aggregates with diameters from 60 to 300 nm, dependent on the arm number and length of star copolymers.

60
Lemonade as a reach source of antioxidants: Polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in lemon extract

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Keywords: lemon extract, ascorbic acid, citric acid, ARGET ATRP, DMAEMA

Increasing concern for the environment leads to the development of novel concepts of manufacturing eco-friendly and profitable polymers. The challenge could be assisted by atom transfer radical polymerization (ATRP) techniques, which are becoming more widespread in the field of polymer chemistry for receiving predetermined structures designed for specific applications. Therefore, in our research, we used freshly squeezed lemon extract for the polymerization of 2-(dimethylamino)ethyl methacrylate by activator regeneration and electron transfer (ARGET) ATRP concept. Lemon delivers a lot of bioactive compounds playing a role of reducing agents in ATRP, e.g., vitamin C or citric acid. It is an environmentally friendly concept and can be scaled up to the industry by using of aqueous reaction medium (instead of organic solvents) and natural reducing agents (instead of laboratory-grade chemicals).

61
Low ppm ARGET ATRP in a cup of coffee

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Keywords: caffeine, DMAEMA, dually-controlled reducing mechanism, ARGET ATRP, aqueous medium

The coffee beverages were tested as a reaction environment for activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) without an additional reducing agent. Two blends were selected: pure Arabica beans and proportional blend of Arabica and Robusta beans. The use of the solution received from the mixture with Robusta allowed obtaining a high molecular weight of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) in a short time, while maintaining a controlled structure of the synthesized product. The proposed concept was carried out at different concentrations of coffee grounds, followed by the determination of the molar concentration of caffeine in applied beverages using DPV and HPLC techniques.

62
Biological application of magnetic particles with polymeric shells containing cholesterol moieties

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Keywords: polymer-iron oxide particles, smart drug delivery system, cholesterol, doxorubicin, anticancer activity

The synthesis and biological application of magnetic polymer-inorganic hybrids containing cholesterol derivatives will be presented[1]. Iron oxide nanoparticles were synthesized according to René Massart's[2] method and modified in a three-step synthetic route to obtain dithiocarbonate-functionalized iron oxide particles (MNP@X)[3]. MNP@X particles were used as chain transfer agents in RAFT (reversible addition-fragmentation chain transfer) polymerizations of *N*-isopropylacrylamide (NIPAAm) or *N*-vinylcaprolactam (NVCL). Then, block co-polymerizations with the synthesized cholesteryl acrylate (CholA) were performed[4]. The obtained materials were characterized by infrared spectroscopy, dynamic light scattering, thermogravimetric analysis, and transmission electron microscopy. Eventually, the particles were tested for anticancer activity.

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63
Isosorbide-based polysebacates as key components for *in situ* forming parenteral drug delivery systems

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Keywords: in situ forming implants, isosorbide, polyesters

In this work, polyesters based on sebacic acid, isosorbide and optionally 1,2-propanediol were synthesized by polycondensation method in the presence of Novozyme 435® as catalysts, and characterized. Poly(isosorbide sebacate-co-1,2-propylene sebacate) (PISEBPG) was chosen as a basic component of new in situ forming implants (ISFI) dedicated to controlled release of doxycycline hyclate (DOXY). Selected properties of new ISFI formulations were investigated in relation to their composition.

64
Responsive polycations with hydrophobic counterions

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This presentation discusses a polycation poly(vinylbenzyl trimethylammonium triflate), PVBTMA, and its block copolymers with PEG. The counterion is hydrophobic triflate, which reduces the solubilities of the polymers, and in aqueous triflate solutions they show UCST behavior. The phase separation process upon cooling aqueous PEG-PVBTMA-OTf is complicated and strongly dependent on the length of the cationic block. When the polymers phase separate, particles are formed. The mechanism of colloidal stability depends on the cationic block length.

A soluble chloride of the polycation has been used as a macroinitiator in PISA polymerization of diacetone acrylamide (DAAM). A whole spectrum of particle morphologies was obtained simply by adjusting the salt (NaCl) concentration. In aqueous triflate solutions the PVBTMA chains on particle surfaces respond to temperature, and interestingly, under certain conditions they show two-step transitions.

65
Synthesis of new oligoesterdiols based on waste poly(ethylene terephthalate) and dimerized fatty acid

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Keywords: poly(ethylene terephthalate), dimerized fatty acid, degradation, oligoesterdiols, resins

New stable binders of organic coatings were obtained by degradation of poly(ethylene terephthalate) (PET) by oligoesterdiols based on dimerized fatty acid (DFA). The number of syntheses were carried out in order to determine how the qualitative and quantitative composition of individual reagents affects the properties of the obtained binder: tendency to crystallize over time, viscosity, glass transition temperature, average molecular weight, dispersion. Two-stage degradation of waste PET by using oligoesterdiols based on dimerized fatty acid and diethylene glycol allowed to obtain stable resins. They were characterized by low glass transition temperature in the range of -46 to -57ºC and relatively low viscosity from 720 to 2420 mPa•s. It was possible to use them as binders in polyurethane coatings. The resulting

66
Visible light-induced photopolymerization of Deep Eutectic Monomers, based on methacrylic acid and tetrabutylammonium salts with different anion structures

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Keywords: deep eutectic monomers, radical polymerization, hydrogen bonds

In our research, we examined the impact of anion in quaternary ammonium salts on the photopolymerization of methacrylic acid (MAA). Four ammonium salts with different anions and the same cation (tetrabutylammonium chloride, tetrabutylammonium bisulfate, tetrabutylammonium nitrite and tetrabutylammonium tetrafluoroborate) forming Deep Eutectic Monomers with MAA were investigated. As a part of the study, we examined structure of DES by means of NMR and, FTIR spectroscopy, changes in density and viscosity for composition with different molar ratios acid to salt. In addition, we determined the conversion curves via RT-FTIR experiments to determine of changes in the initial rate of polymerization.

67
Non-isocyanate aliphatic and aliphatic-aromatic poly(carbonate-urethane)s based on dimethyl dicarbamates

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Keywords: non-isocyanate polyurethane, non-phosgene polyurethane, polycondensation, carbamates, oligocarbonatediol

Polyurethanes (PURs) are among the most widely used polymers due to their unique structure and properties. They are applied as foams, sealants, adhesives, and biocompatible materials.

This report presents a non-isocyanate synthesis method of aliphatic and aliphatic-aromatic PURs via the transurethanization of dimethyl dicarbamates with α,ω-diol and then polycondensation between obtained urethanediol and oligocarbonate diol as an alternative to the use of toxic diisocyanates.

The structure of the obtained non-isocyanate PURs was studied using ^{1}H and ^{13}C NMR, FT-IR spectroscopy, and MALDI-ToF mass spectrometry. Obtained aliphatic and aliphatic-aromatic PURs exhibited similar mechanical properties to typical isocyanate-based PURs – the tensile strength above 40 MPa (aliphatic PURs) and up to 50 MPa (aromatic PURs).

68
Synthesis of branched polycaprolactone

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Keywords: polycaprolactone, branched polymers, biodegradable

Polycaprolactone (PCL) belongs to the group of biodegradable polyesters. It is widely used as a biomaterial, but also in the polymer industry. The polymerization of caprolactone proceeds by ring opening polymerization with the addition of an initiator, which may have a beneficial effect on the polymerization process and on the product properties. An innovative approach in the research of these compounds is using hyperbranched polymers (HP) as caprolactone polymerization initiators. Incorporating branches into the structure of the polymer improves solubility, increases the amount of free functional groups, and reduces viscosity in solution and in molten state, compared to linear polymers. The research presented in this study concerns the synthesis of polycaprolactone with various hyperbranched macroinitiators, carried out using an organometallic catalyst. The obtained products were characterized by methods such as ^{1}H NMR and GPC. The results of the synthesis and the analyzes performed are compared in this study.

69
Towards visible light! The new photoinitiators for light-induced cationic photopolymerization – challenges and opportunities

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Keywords: visible light, cationic, photopolymerization, photoinitiators

The growing interest in photopolymerization systems based on the cationic mechanism encourages searching for new types of cationic photoinitiators because their properties determine the efficiency and rate of photopolymerization.

The matching of the absorption characteristics of the initiators to the emission characteristics of Vis-LED lamps will enable better utilization of energy by increasing the photolysis rate of iodonium salts, thus increasing the initiation rate of the photopolymerization process. Real-time FT-IR was used to monitor the photopolymerization processes for epoxy and vinyl monomers. The spectroscopic characteristics of photoinitiators investigated, their photostability, and their efficiency in generating strong protic acid during photolysis was determined.

It has been shown that all the investigated derivatives show effective action when a Vis-LED type light source of visible range with maximum emission of λ_{max} = 405 nm and λ_{max} = 420 nm is used.

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70
Properties and structural changes of bacterial polymer levan as a functional coating material for biomedical applications

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Keywords: levan, magnetic nanoparticles, photodegradation, photosensitizer, singlet oxygen

This study presents the synthesis and properties of advanced nanomaterials in which the advantage features of the magnetic nanoparticles and photoactive compounds were combined. This work's primary purpose was to synthesize magnetic nanoparticles coated with biocompatible and antitumor polysaccharide – levan and the deposition of potent photosensitizer – zinc(II) phthalocyanine on their surface. In order to better characterize the nature of the coating covering the magnetic core, the atomic force microscope analysis, a contact angle measurement, and the mechanical properties of pure levan and its blend with zinc(II) phthalocyanine films were investigated. Moreover, the effects of irradiation LED and polychromatic lamps on the structural properties of levan were also studied. This magnetic nanomaterial revealed the ability to generate singlet oxygen upon exposure to light.

71

Formation and properties of nanoparticles by poly(oligoethylene glycol) methacrylates with degradable oligoester units

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Keywords: methacrylates, oligolactide, ATRP, thermoresponsive materials, nanoparticles

The main aim of the research was to obtain nano- and microparticles based on oligo(ethylene glycol) methacrylates. For this purpose, thermosensitive copolymers of P((TEGMA-EE)-co-($OEGMA_{300}$)-co-($HOEGMA_{360}$))-graft-lactide with double bond derived from the acrylic group were synthesized. The obtained polymers were thermoresponsive with T_{cp} from 30°C to 50°C, which could be controlled by the length of the oligolactide chain, comonomer composition and the presence of a double bond. The introduction of acrylic groups into the chain made it possible to obtain stable particles in dilute aqueous solutions, above T_{cp}. The formed particles ranged in size from 100 nm to 800 nm and were degraded over time. The presence of the degradable fragment in the obtained polymer particles makes the obtained particle possible to be use as drug delivery systems. The gradual release of the encapsulated active substance should depend on the degree of polymer degradation with time.

72
The thermoresponsive behaviour of N-isopropylacrylamide copolymer with 2-acrylamidephenylboronic acid in aqueous solution

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In this work we present the phase behaviour of statistical N-isopropylacrylamide, NIPAM copolymers with 2-acrylamidephenylboronic acid, 2-AAPBA in aqueous solutions , which was investigated with UV/Vis spectrometry, DLS, DSC, and ^{1}H NMR spectroscopy. The presence of 2-AAPBA in the NIPAM copolymers significantly influenced the thermoresponsive behaviour of PNIPAM. As expected, the cloud point of copolymers slightly increased in comparison to PNIPAM, up to 37°C at 30 mol% of 2-AAPBA content, which is related to the increased hydrophilicity of the synthesized copolymers. The cloud point for P(NIPAM-co-2-AAPBA) copolymers with a 2-AAPBA content exceeding 30 mol% is no longer observed. In the case of P(NIPAM-co-2-AAPBA) copolymers with a 2-AAPBA content between 5 and 30 mol%, the unexpected increased hysteresis in the mixing/demixing temperature was observed upon a heating and cooling cycle. The NIPAM copolymer with 5 mol% 2-AAPBA content displayed the hysteresis reaching 5°C. A further increase of 2-AAPBA in the copolymer led to the gradual broadening of its range reaching 25°C for the aqueous solution of NIPAM copolymer with 30 mol% of the molar fraction of 2-AAPBA. Moreover, DLS experiments carried out for this copolymer showed the formation of nanoparticles over the cloud point that swell below 30°C, however, did not disassemble upon cooling even down to 5°C. Thus, these particles have the potential as nanocarriers for drug delivery applications. The occurrence of the hysteresis was explained by the formation of boroxine motifs as an effect of the dehydration of boronic acid moieties upon heating. Raman spectra recorded for NIPAM copolymer with 15 mol% 2-AAPBA content below and above the cloud point, respectively, revealed over the cloud point the appearance of a vibrational band at 753 cm^{-1} characteristic of boroxine, i.e., boronic acid anhydride. The detailed analysis of experimental data supported with DFT calculations evidenced the presence of other vibrational bands of 2-AAPBA anhydride (780, 957 and 999 cm^{-1}).

This study demonstrates the potential of the 2-AAPBA comonomer for the fabrication of self-healing/recyclable boroxine-based polymer networks.

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73
Formation of nanostructures by hydrophobically modified chondroitin sulfate

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Keywords: chondroitin sulfate, amphiphilic self-assembled nanoparticles, molecular dynamics simulations, curcumin

Drug delivery systems (DDSs) based on polymer nanoparticles have many benefits, including improving the therapeutic properties of drugs. Natural polysaccharides such as chondroitin sulfate (CS) are being intensively researched to develop nano-scale DDS systems. In this study, the amphiphilic derivatives of CS were synthesized and their behavior in the water phase was investigated. In particular, the focus was on the hydration of the polysaccharide backbone, the influence of the degree of substitution with hydrophobic groups on the aggregation capacity of the amphiphilic CS. The morphology of the nanostructures and their molecular organization were investigated using electron microscopy imaging and computer simulations. Then, several experimental methods and molecular dynamics simulations were used to determine the suitability of the obtained polymer structures as drug carriers. Curcumin was used as a model drug.

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74
Ciprofloxacin loaded mixed polymeric micelles for destruction of bacterial biofilms

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Keywords: polymeric micelles, drug delivery, bacterial biofilms

Polymeric micelles have been extensively studied as drug delivery carriers. In the recent years various micellar systems carrying a positive charge have been found to exhibit strong antibacterial activity. Since the polycations are usually associated with pronounced cytotoxicity mixed polymer micelles bearing non-ionic moieties might be a good alternative for development of novel biocompatible anti-biofilm agents.

In this work loading of Ciprofloxacin into polymeric micelles of different composition was investigated. Polymeric micelles were formed from cationic poly(2-(dimethylamino)ethyl methacrylate)-b-poly(ε-caprolactone)-b-poly(2-(dimethylamino)ethyl methacrylate) and non-ionic poly(ethylene oxide)–b-poly(propylene oxide)–b-poly(ethylene oxide) triblock copolymers as well as from their mixtures at different molar ratios. The encapsulation efficiency, drug loading content and drug release profile of polymeric carriers were determined. A cytotoxicity evaluation of the resulting drug delivery systems was performed. The biomass reduction of pre-formed bacterial biofilms was estimated as well as their metabolic activity.

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75
Self-assembled micellar nanoparticles of a novel betulin based polyanhydrides

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Keywords: betulin, polyanhydrides, micelles, graft copolymers

Polymeric micelles are nanoscopic core/shell structures formed by amphiphilic block or graft copolymers. They are extensively studied carriers for the poorly water-soluble drugs. The most commonly used hydrophilic segment of micelles for drug delivery is poly(ethylene glycol) (PEG). In this work, new amphiphilic polyanhydrides were obtained from betulin disuccinate (DBB) and trifunctional PEG, terminated with carboxyl groups. DBB has a broad spectrum of biological activity, thus it seems to be promising as new, therapeutic agent. DBB based polyanhydrides release the DBB as a result of hydrolytic degradation in physiological condition and exhibit anti-cancer activity, thus they can be used as a polymeric prodrug. Due to their biodegradability and non-toxicity, they are also ideal candidates for carriers of other biologically active substances. The aim of this work was to verify the suitability of such polymers for micelles formation in self-assembling processes.

76
Dual-targeted PLA-PEG micelles for anticancer drug delivery

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Keywords: polymeric micelles, active targeting, folic acid, biotin, docetaxel

Conventional chemotherapy may cause many severe side effects - the serious problem of intravenous systemic chemotherapy is the unspecific targeting to the tumor and difficulties to achieve therapeutic level of drug within or adjacent to the tumor. According to the most recent recommendations, future nanomedicine should be focused mainly on active targeting of nanocarriers based on ligand-receptor recognition, which may show better efficacy than passive targeting in human cancer therapy. The aim of the study was to develop biodegradable micelles from block polymers functionalized with folic acid and biotin. The micelles were loaded with docetaxel as an anticancer drug. Drug loading properties and *in vitro* release kinetics were analyzed. Morphology of micelles was observed using TEM. The anticancer properties of the nanocarriers were tested under *in vitro* conditions against cancer and normal cell lines.

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77
pH-sensitive nanoparticles base on pentane-1,3,5-triol and citric acid

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Keywords: nanoparticles, pentane-1,3,5-triol, citric acid, carriers

Sub-micron sized particles have recently gained a lot of attention for developing advanced drug delivery systems. In this contribution, we report the synthesis of novel biodegradable nanoparticles from two natural products – citric acid and pentane-1,3,5-triol, a by-product of lignocellulose processing. The particles were obtained by the Steglich esterification method at room temperature with N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide (EDC) and 4-dimethyl aminopyridine (DMAP) catalyst system. Dynamic light scattering study revealed a mean hydrodynamic diameter of 111 nm and a negative zeta potential -8 mV. The carboxylic groups present in the particles can be exploited for complexing with positively charged bioactive substances.

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78
Degradation of poly(sebacic acid) microparticles loaded with azithromycin as pulmonary drug carriers

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Keywords: degradation, microparticles, pulmonary drug delivery

Recurrent bacterial lung infections are difficult to treat due to increasing bacterial resistance to antibiotics. Novel inhalable drug carriers can potentially improve treatment efficacy via increased drug bioavailability and reduction of bacterial exposure to antibiotics.

The microparticles based on poly(sebacic acid) loaded with azithromycin (MPs) were manufactured using oil-in-water emulsification/solvent evaporation method. The MPs were spherical and slightly porous, with diameters between 1 μm and 5 μm. Rapid degradation of the MPs in phosphate buffered saline (PBS) at 37°C was evidenced by a decrease in the buffer pH, weight loss of the MPs, and changes in their morphology.

Further studies including evaluation of MPs cytotoxicity and antibacterial properties are indispensable, but the developed MPs have great potential as pulmonary drug carriers.

79
Simplified production of ultra-fine silicon nanoparticles through economical chemistry

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Keywords: Si nanoparticle, ultra-fine silicon, trichlorosilane, synthesis

Silicon nanoparticles (Si NPs) are of great interest to scientists due to their unique size-dependent electronic and optical properties. Currently, one of the most desirable Si NPs for use in microelectronic devices, light-emitting diodes (LEDs), photopumped tunable lasers and in sensors are ultra-fine Si NPs with diameters below 10 nm. We report a simplified synthesis protocol for ultra-fine silicon nanoparticles which has the advantage of being safer and cheaper than most other approaches and without the need for a Schlenk vacuum line. The process involves the production of a (HSiO1.5)n sol-gel precursor based on the polycondensation of low-cost trichlorosilane (HSiCl3), followed by its annealing and etching. Fourier transform and Raman spectroscopy, X-ray dispersion spectroscopy as well as microscopy characterizations (SEM, TEM) confirm the formation of crystalline ultra-fine Si NPs with controllable mean diameters ranging from 1 to 5 nm depending on the etching time. The obtained material was also studied for its photoluminescent properties.

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80
Micellar structures based on ionic graft copolymers for antituberculosis drug delivery

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Keywords: in vitro drug release, micelles, carriers, graft copolymers

In order to overcome drawbacks associated with an conventional usage of drugs, targeted drug delivery systems are investigated. One of the studied are the polymeric micellar systems. They offer protection of a drug during transport and enhanced control of its release.

In present research the ionic graft copolymers containing various content of choline chloride in side chains (25 or 50%) were used as a polymer matrix to obtain micellar structures. Critical micelle concentration (CMC) was determined by goniometer method (CMC = 0.011-0.020 mg/mL), what confirmed amphiphilic character of tested compounds. Encapsulation of bactericidal antibiotic, i.e., Rifampicin (RIF), led to high content of RIF in micelles (DLC = 41-67%). The *in vitro* release studies were carried at PBS for 50 h, (pH = 7.4, 37^{o}C) resulting in 20-36% (10-17 μg/mL) of free drug. Results showed that presented graft copolymers are promising candidates for drug delivery.

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81
Magnetic nanoparticles coated with starch enriched in dihydroxyboryl groups for the immobilization of glycoproteins

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Keywords: magnetic nanoparticles, starch, boronic acids, immobilization, glycoprotein

The main objective of the research was to obtain magnetic nanoparticles coated with chemically modified biopolymers that will have highly reactive functional groups capable of effectively immobilizing glycoproteins without losing their ability to bind active substances. The first phase of the project involved the synthesis of starch-coated magnetic nanoparticles by in situ co-precipitation. In the next step, the polymer was chemically modified, which led to the production of dialdehyde starch, which was then coupled with 3-aminophenylboronic acid. The obtained materials consist of a magnetite core covered with starch enriched in dihydroxyboryl groups. The obtained materials were fully characterized (scanning electron microscopy, transmission electron microscopy, XRD, thermal analysis and ATR-FTIR analysis). The obtained materials were used for the immobilization of acid α_1-glycoprotein.

82
Comparison of micellization process of linear polystyrene-b-polyglycidol and coil-brush polystyrene-b-(polyglycidol-g-polyglycidol) copolymers

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Keywords: block copolymer, brush copolymer, aggregation, nanoparticles, cryo-TEM

In the last years amphiphilic block copolymers are widely studied for the use in controlled drug delivery systems [1, 2], carriers of biological markers [3] and many others. For the purpose of this work set of amphiphilic polystyrene-b-polyglycidol (PS-b-PGL) diblock copolymers and polystyrene-b-(polyglycidol-g-polyglycidol) PS-b-(PGL-g-PGL) coil-brush copolymers with similar molar mass and composition were prepared via anionic polymerization.

The self-assembly process of studied copolymers in water were investigated. The critical concentration of self-assembly were observed by dynamic light scattering (DLS). Linear increase of critical concentration with increasing content of hydrophilic glycidol units in the copolymer chain were observed. The size parameters of the aggregated structures were determined using DLS. Cryogenic transmission electron microscopy images revealed the presence of spherical objects and confirmed their sizes**.**

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

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83

Effect of the microstructure of poly(L-Lactide-co-glycolide) microsphereson cell proliferation and differentiation for modular tissue engineering application

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Keywords: microspheres, PLGA, polymeric cell carrier, modular tissue engineering

The human body has the ability to regenerate itself, but in the case of extensive damage, some disease, or advanced age, these possibilities may be limited or even impossible. The aim of the study was to create microspheres from resorbable poly(L-lactide-co-glycolide) (PLGA MS) by single oil/water emulsification and to evaluate the possibility of using them as cell carriers, which can be used as building blocks in the modular tissue engineering . PLGA MS were characterized by optical microscopy, and their surface, shape, and size were measured. Biological evaluation was performed with osteoblast-like MG-63 cells on 1, 3, 7, and 14 days after starting cell culture. Live/dead staining, LDH test, and ALP concentration were performed for morphology, proliferation, and mineralization assay, respectively. The results showed that PLGA MS promote cell proliferation, and, more importantly, the mineralization is higher than for the controls.

84

Radioisotope nanocarrier systems for cancer theranostics based on radiation-synthesized polymer nanogels

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Keywords: cancer theranostics, radiopharmaceuticals, nanogels, nanotechnology, ionizing radiation

Ionizing radiation has been demonstrated to be an efficient tool to synthesize polymer nanogels in a pure polymer-water system, using no initiators, surfactants, crosslinking agents or other additives. In this work radiation-synthesized nanogels of poly(acrylic acid) are used for controlled targeting of radioisotopes, thus forming nanoradiopharmaceuticals for diagnostics and treatment of cancer. Optimization of synthesis and handling has been followed by derivatization with targeting agent and radioisotope-binding ligands. Cell culture tests yielded positive results and the project is currently moving into the phase of animal studies.

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85
Drug delivery systems based on hydrophobically modified chondroitin sulfate

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Keywords: biopolymers, chondroitin sulfate, polymeric nanoparticles, drug delivery

Chondroitin sulfate (CS) is a natural polysaccharide found in living organisms. Due to its biocompatibility and biodegradability, it is considered a biomaterial for the development of nanoscale drug delivery systems (DDSs). In this work, nanostructures from hydrophobically modified CS were prepared and studied their morphology and sizes using dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM). Subsequently, the possibility of converting these structures into drug (curcumin) delivery systems was tested, the binding constant (K_b), drug loading capacity (DLC), and encapsulation efficiency (EE) were determined.

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86
Safe and effective polymeric Zika virus inhibitors

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Keywords: zika virus, amphiphilic copolymers, self- organization, nanoparticles

Amphiphilic copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) and sodium 11-(acrylamido)undecanoate (AaU), both block and random, were obtained via RAFT and FRP, respectively, and demonstrated to act as very efficient and safe agents against Zika virus (ZIKV). The macromolecules of these polymers undergo self-organization in aqueous media with formation of negatively charged (ζ= −25 mV) nanoparticles (4-12 nm). They inhibit the ZIKV replication by binding to the host cell surface, thereby blocking virus attachment to cells. Considering good solubility in aqueous media, low toxicity, and high selectivity index (SI) of the PAMPS-*b*-PAaU copolymers, they can be considered promising agents against ZIKV infections.

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87
Synthesis of novel polycaprolactone/polyglycidol based block and star copolymers for development niosomes

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Keywords: click chemistry, niosomes, polycaprolactone, polyglycidol

Recently one of the fastest growing areas in the modern pharmaceutical science and technology is targeted drug delivery. The practical realization of this concept is possible thanks to recent advances in nanotechnology. In the field of nanoscale drug carriers, niosomes attract increasing scientific interest as promising drug delivery systems. They are composed of nonionic surfactants and cholesterol and offer several advantages as vesicles for drug encapsulation, codelivery of lipophilic/water insoluble and hydrophilic compounds, biocompatibility, low-immunogenicity, stability (physical, chemical and osmotic) and controlled release and targeting properties. By adding appropriately designed polymers, the membranes of niosomes can be modified. This strategy offers many possibilities for fabricating highly effective carriers which, in addition, can release the incorporated drugs in a controlled manner. In this regard, a series of linear block and star copolymers based on polycaprolactone/polyglycidol were synthesized and characterized in detail using "click" chemistry reactions. Novel noisome formulations were prepared using various surfactants and polycaprolactone/polyglycidol and characterized in terms of size, size distribution, and morphology.

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88
Novel amphiphilic polyglycidol/poly(ε-caprolactone) and polyglycidol/poly(α-cinnamyl-ε-caprolactone) copolymers as highly effective nanocarriers

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Keywords: click chemistry, polyglycidol, poly(ε-caprolactone), copolymers, functional nanomaterials

Recently drug delivery systems based on amphiphilic block copolymer nanoparticles have focused much attention for controlled delivery of biological active substances (low-molecular-weight drugs, enzymes, DNA, and RNA). Amphiphilic block copolymers frequently self-assemble in aqueous media into nanosized, spherical, core-shell micelles. Recently for the synthesis of well-defined block copolymers, the highly efficient "click" chemistry reactions are preferred. In this work by applying the azide-alkyne cycloaddition, novel linear block copolymers comprising PEEGE (protected PG) and poly(ε-caprolactone) or poly(α-cinnamyl-ε-caprolactone-co-ε-caprolactone)) was successfully obtained. Further, we report on the preparation, physicochemical and biological characterization of well-defined nano-sized micellar carriers loaded with cannabidiol (CBD) and the effect of pendant cinnamyl moieties on the cytotoxicity and encapsulation efficiency of the natural bioactive compound caffeic acid phenethyl ester (CAPE).

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89
Nucleolipid vesicles: Supramolecular structures resembling spherical nucleic acids

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Keywords: nucleolipids/oligonucleotides, vesicles/liposomes, spherical nucleic acids, click chemistry, light scattering, cryo-TEM

An original nucleolipid, composed of a hydrophobic residue, resembling that of the naturally occurring phospholipids, and a DNA oligonucleotide strand is synthesized by coupling of dibenzocyclooctyne-functionalized oligonucleotide and azidated 1,3-dihexadecyl-propane-2-ol via an azide-alkyne *click* reaction. The nucleolipid is amphiphilic and in aqueous solution spontaneously self-associates into nanosized supramolecular structures, identified as unilamellar vesicles composed of a self-closed *interdigitated* bilayer. Vesicular structures are also formed upon intercalation of the nucleolipid via its lipid-mimetic residue in the phospholipid bilayer membrane of liposomes prepared from readily available and FDA-approved lipids. The constructs are spherical in shape, relatively small in size (R_h = 66.6 nm), moderately negatively charged (ζ = -17.8 mV), and carry thousands of DNA strands grafted on the bilayer membrane. The dense functionalization not only stabilizes these constructs but also provides enhanced nuclease stability and facilitates cellular internalization.

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90
Polymer nanocapsules templated on liquid cores as a model photoreactors

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Keywords: polymer nanocapsules, oil cores, nanoreactors

Confined environments of nanoreactors allow to carry out efficient and selective chemical reactions. Here, we report simple, one-step technique for preparing nanocapsules with oil, liquid cores. These capsules were stabilized by amphiphilic polyelectrolytes with comb-like graft architecture. We show that the polymer nanocapsules can be simply loaded with reactants and a model reaction of photooxidation of perylene encapsulated in their cores can be successfully in an aqueous dispersion of the capsules.

Physicochemical properties of the obtained polymeric capsules were investigated by dynamic light scattering measurements, long term stability was confirmed with zeta potential measurements, and morphology of the capsules was revealed with scanning electron microscopy. The ability to encapsulate hydrophobic compounds was confirmed by confocal microscopy

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91
Polymer electrolytes for lithium-ion batteries

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Keywords: polymer electrolytes, lithium-ion, 3D printing, SPE, GPE

The most common **power sources** in mobile devices and electric cars are **lithium-ion batteries**. Unfortunately, among the many advantages such as high specific capacity and current density, lithium-ion cells have one main disadvantage – **low safety of use**. Most lithium-ion batteries contain liquid electrolytes containing volatile and flammable organic solvents, which can be dangerous especially in the event of unsealing battery (e.g. in a car accident) leading to fire or explosion. Our research is focused in obtaining polymer electrolytes that do not contain liquids components (**solid polymer electrolytes** – SPE) or contain liquid electrolyte trapped in a crosslinked polymer network (**gel polymer electrolytes** – GPE). Polymer electrolytes obtained by our group can be formed using 3D printing techniques, leading to the manufacture of electrolytes of custom shape, precisely suited to the shape of the electrodes and the individual requirements of the end user.

92
Modified flame-retardant nonwoven RPET for acoustic protection

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Keywords: RPET nonwoven, flame-retardancy, impregnation, acoustic protection

The main way of utilizing poly(ethylene terephthalate) waste is through material recycling. Waste bottles and containers are processed into RPET regranulate, which is then used to manufacture various types of products, including thermal insulation nonwovens. Raw nonwovens produced from recycled PET fibers are characterized by low ignition resistance. In order to ensure the possibility of using these materials in construction industry, it becomes necessary to carry out modifications of their flammability properties. One of the possible ways of obtaining an increased degree of flame-retardancy is impregnation. In this paper, the use of sodium water glass for impregnation of thermo-insulating PET nonwoven fabric intended also for acoustic protection has been proposed.

93
Flame-retarding modification of PET fibers with montmorillonite Cloisite 30B

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Keywords: PET fibers, flame-retardant modification, LOI, TGA

Standard PET fibers are not very resistant to fire and large amounts of smoke are emitted during their combustion. In addition, the so-called dripping effect is observed, detached drops of molten polymer burn and promote the spread of fire. The flame-retarding modification of PET fibers can be carried out in various ways. Most often, a properly ground anti-pyrene is added to the polymer melt.

The alternative method to reduce the flammability of PET fibers, analogous to dyeing of PET fibers with dispersed dyes in a high-temperature bath was proposed. A commercial organophilic montmorillonite Cloisite®30B was applied as a flame-retardant. The aim of the presented work was to evaluate the effectiveness of the introduced modifier and the improvement of the flame-retardant properties of PET fibers by LOI and TGA measurements.

94
Thermochromic polyethylene materials

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Keywords: polyethylene, thermochrome, colorful concentrates

In everyday life, plastics that reversibly change color under the influence of temperature variations are becoming more and more popular. My interests include polyethylene with the addition of thermochrome – a substance capable of reversible or irreversible color changes as a result of different temperature. Thermochromism can occur in various classes of polymers, e.g. thermoplastic, thermosets and also in gels, inks or paints. The appropriate selection of a polymer, dye or pigment has a decisive impact on obtaining a thermochromic material with the desired properties. A very important factor is also adjusting the processing parameters in the injection or extrusion method.

95
An experimental study on extrusion of a material based on chitosan and starch simulated in Haake Rheomix Lab Mixer

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Keywords: chitosan, starch, extrusion, thermomechanical processing, biopolymers

Nowadays, there is a growing interest in biodegradable and compostable polymers. One of the greatest hurdles of the biopolymer materials– in this case chitosan/starch-based, is their production and the time elapsed in the process. In this study, chitosan/starch-based materials modified with lignin and poly(vinyl alcohol) have been successfully prepared in a Haake Rheomix Lab Mixer via thermomechanical processing. Different contents and types of lignin and poly(vinyl alcohol) were incorporated into the chitosan/starch compositions to improve their processing and physicochemical properties. The performed study proved that extrusion is a suitable method for obtaining a thermomechanical processed material based on chitosan and starch. Due to the fact that extrusion is the most popular method used in the production of packaging, the presented studies can contribute to broadening the applicability of biopolymers at a large scale.

96
Polymeric barrier materials (gloves) – study of mechanical properties

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Keywords: nitryle gloves, gloves in medical application, mechanical properties, barrier materials

The work was devoted to the physico-mechanical analysis of barrier materials used in the medical sector in order to compare their properties. Seven types of gloves currently available on the market for medical applications were selected for the study. The selection was made on the basis of sales reports and positive user feedback. The tests of mechanical properties using the static tensile test method were carried out on the universal testing machine INSTRON 5982, in accordance with the applicable PN-EN ISO527-3 standard. The thickness and the surface morphology of the gloves (using SEM) was also measured.

97
Nonterminal LC epoxy resin with exceptionally low glass transition temperature

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Keywords: thermoset, thermal analysis, DSC, liquid crystal, curing

The novel liquid crystalline epoxy resin with a three-aromatic ring core and epoxy groups in the middle of the aliphatic chains was synthesized and subjected to curing with aromatic amines as hardeners. Differential scanning calorimetry analyzes showed a wide temperature range of the curing reaction and its low intensity measured by the reaction enthalpy in most of the examined thermosetting compositions. However, the most valuable result is an exceptionally low glass transition temperature often placed below room temperature. It allows to achieve a cured liquid crystalline system with the possibility of utilization as the unique rubbery-state smart material with possible conducting properties provided by the mesogenic core.

98
MIL-53(Al) to fabricate high-performance hybrid membranes with enhanced selectivity for organic-organic pervaporation

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Keywords: organic-organic pervaporation, MOF particle, membrane modification, Mixed Matrix Membranes

Dimethyl carbonate (DMC) is a biodegradable and practically non-toxic solvent, a fuel additive. As this compound is produced from methanol (MeOH), energy-efficient breaking of the azeotrope is vital for economic production. Pervaporation is well known as a good tool for breaking azeotrope.

The aim of this research was to evaluated and modified by incorporation of various amounts of MIL-53(Al) poly(dimethylsiloxane) based membranes for the separation of DMC from DMC/MeOH mixtures.

The physicochemical properties of prepared membranes were determined by applying SEM, AFM, TGA analysis. Pervaporation results were analyzed implementing separation factor (β) permeate fluxes (J_i), and thickness normalized Pervaporation Separation Index (PSI_N).

99
Elastic substrates based on polymers for organic electronics applications

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Keywords: polymer substrates, thermal characterization, electronics applications

The recycling of polyethylene terephthalate (PET) is one of the most current topics in the processing of polymer materials. Great opportunities are created by the possibility of making inert (or coloured) substrates for the needs of organic electronics. Based on various admixtures of polymer materials (as recycled materials), the harmful impact on the environment is minimized. Researching this area allows for the preparation of substrates with specific properties (e.g. appropriate glass transition temperature, optical properties in the UV-Vis range or resistivity). The research are financed by The National Centre for Research and Development (NCBiR) under grant LIDER XI no. LIDER/39/0137/L-11/19/NCBR/2020.

100
3D reactive inkjet printing of aliphatic polyureas using in-air coalescence technique

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Keywords: 3D printing, reactive inkjet, polyuria

An in-flight coalescence reactive inkjet printer has been developed to facilitate the in-air collision of two reactive microdroplets. This way precise volumes of reactive inks can be mixed and subsequently deposited on the substrate to produce the desired product by polymer synthesis and patterning ina single step. We validate the printer capabilities by fabrication of a series of 3D structures using an aliphatic polyurea system (isophorone diisocyanate IPDI and poly(propylene glycol) bis(2-aminopropyl ether) PEA-400). The influence of temperature and ink ratio on the material properties has been investigated. An increase in both IPDI and temperature facilitates the production of materials with higher Young's Modulus E and higher tensile strength σ. The possibility of printing different materials i.e. ductile (σ=2 MPa, ε=450%), quasi-brittle (σ=14 MPa, ε=350%), and brittle (σ=10 MPa, ε=11%) by varying the printing process parameters using one set of inks has been presented.

101
Novel synthesis of monoazo hybrid pigments on aminosilane functionalized silica supports

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Keywords: azo dye, elastomer composite, fumed silica, organic-Inorganic hybrid, pigment, silane

This research sets out to develop a novel method for the synthesis of organic-inorganic structures, based on compounds containing silicon and organic chromophores. The surface fumed silica Aerosil 380 was modified using three aminosilanes with different numbers of amino groups (e.g. (3-aminopropyl)triethoxysilane), to obtain functional groups on the surface. Silica functionalization enabled effective binding to an azo-chromophore, resulting in the formation of an organic-inorganic pigment with a vivid red colour. The ^{1}HNMR, elemental analysis, scanning electron microscopy and FTIR, colorimetric and solvent resistance tests were performed. Presented process resulted in a series of organic-inorganic colorants. Obtained hybrid pigments were applied as colored multifunctional additives in polymer composites. The application of these pigments as colorants in elastomer material confirmed their high thermal and chemical resistance during NBR rubber vulcanization.

102
New shear-thickening electrolytes for lithium-ion batteries with increased safety

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Keywords: shear-thickening electrolyte, lithium-ion battery, star-shaped oligomer, safety

Lithium ion batteries (LIBs) are key components of modern, portable electronic devices. In LIBs, typically used organic solvent-based electrolytes are a major safety concern due to their flammability. One of the methods of improving their safety is the development of systems capable to responding to an impact, such as shear thickening electrolytes. There are many factors to consider while developing systems exhibiting the shear thickening effect, e.g. the size, shape and concentration of ceramic particles, type of functional groups on their surface and properties of organic dispersant. We present here the results of research on electrolytes based on star-shaped oligomers of propylene oxide and ethylene oxide with silica nanoparticles and lithium trifluoromethanesulfonate.

103
Effect of silicone oil on the thermal properties of poly(dimethylsiloxane) (PDMS)

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Keywords: silicone, aging, thermal stability

The aim of the study was to assess the impact of the presence of silicone oil on thermal stability and thermal effects of poly(dimethylsiloxane) PDMS. The influence of the previous aging process and the samples loading on the observed changes was also analysed. Studies have shown that soaking PDMS materials with silicone oil increases their thermal stability. A several-percent reduction in total weight loss is observed in the case of samples soaked in oil, which is particularly noticeable for samples subjected to the previous aging process. The temperature of the last transformation on the DSC curve (T_{DSCmax}) for non-degreased samples also increases significantly. The observed differences suggest that soaking PDMS materials with silicone oil affects the nature of structural changes in the course of their loading and aging, as well as during thermal decomposition.

Acknowledgement: *This work was supported from the Małopolska Regional Development Agency SA as a part of the project 'Knowledge, practice, staff – key to business success' no. MARR/1677/2012/DZPP. Thermal tests were carried out in the Faculty Laboratory of Thermophysical Research, Faculty of Materials Science and Ceramics AGH.*

104
The effect of magnetic field and the morphology of curing agent on properties of liquid crystalline epoxy networks

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Keyword: liquid-crystalline epoxy resins, magnetic field orientation, ordered structure

Liquid crystalline polymer networks (LCPNs) can form systems with excellent fracture and breaking toughness, high modulus, especially in the direction of mesogen orientation, low coefficient of thermal expansion, and mechanical and optical anisotropy. The morphology and properties of LCPN can be modified among others by applying an ordering force field during their curing or by using a crosslinking agent with a different structure. In our work, we synthesized an ordered liquid crystalline epoxy network using liquid crystalline diepoxy monomer containing triaromatic mesogenic group and isomers of phenylenediamine (ortho-, meta-, and para-) as a curing agent. A magnetic field was applied during the cross-linking reaction. As expected, using the magnetic field upon curing, the networks had ordered structures, but their morphology depended on the arrangement of the active groups of $–NH_2$ in the amines used.

105
Porous conductive polymer and reduced graphene oxide composites via hydrothermal synthesis for energy storage applications

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Keywords: reduced graphene oxide, polyaniline, polypyrrole, hydrothermal synthesis, supercapacitors

Hydrothermal synthesis is an environmentally friendly, scalable, and economically wise approach for the synthesis of various nanostructures. We have found that hydrothermal conditions are crucial to obtain conductive polymer-reduced graphene oxide composites with developed porous structure, especially when loading of the nonporous polymer component is high. The already synthesized conductive polymers have been mixed with a graphene precursor with equal mass ratios and have undergone a hydrothermal treatment at high temperature. The BET surface area of the composites was in the range of 228 to 597 m^2/g, while pristine reduced graphene oxide yielded 492 m^2/g under the same conditions. Developed composites were investigated as electrode materials for supercapacitor applications, as good porosity and a high pseudocapacitive polymer component are desirable traits for the best electrochemical performance.

106
Polymers for application in hybrid solar cells

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Keywords: polymers, perovskite solar cells, hybrid solar cells

In the past years, hybrid solar cells are regarded as promising photovoltaic technologies. The components and structures of devices are significant to the devices' stability and efficiency. Due to polymers' unique and diversified properties, they are tested for applications in perovskite solar cells. Polymers are applied as additives to perovskite layer(s) to improve the nucleation and crystallization processes in the perovskite layer(s). The polymers can also be used as electrons and holes transporting materials, due to appropriate both charge mobility and possibility of energy level arrangement, and as an interface layer to reduce the recombination and enhance the carrier separation efficiency. The aim of this work is a presentation of the current achievements concern the applications of polymers in perovskite solar cells.

107
Functionalized Moringa oleifera gum as pH-responsive drug delivery device

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Keywords: moringa oleifera gum, pH-responsive, swelling, kinetic modelling, rhabdosarcoma cells

Herein, *Moringa oleifera* gum-based superabsorbent hydrogel (MOGH) was synthesized via γ-irradiation method using acrylamide (monomer), followed by partial hydrolysis with NaOH, sonication and ultracentrifugation. Swelling studies revealed superabsorbent nature (363 g/g) of MOGN including excellent swelling within the pH range of cancerous cells i.e., 5.0–6.8. MOGN showed a very high uptake (98.35%) of DOX. Drug release kinetics revealed that DOX release from DOX-MOGN followed Korsmeyer-Peppas model at pH 5.5 and 6.8 and Higuchi model at pH 7.4. *In vitro* release studies showed that DOX release was maximum at pH 5.5 followed by 6.8 and 7.4 with %release of 91.92%, 62.62% and 19.33%, respectively, from DOX-loaded MOGH. Efficient DOX release at tumor-site was also confirmed by cytotoxic studies using Rhabdomyosarcoma cells. The optimal DOX release and cytotoxicity studies at pH 5.5 are in consonance. Further studies on *Moringa oleifera* gum application for blending or grafting with PHA to synthesize novel biomaterials are under way.

Acknowledgement: *This research is partly supported by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 847639 and from the Ministry of Education and Science.*

108
Removal of methylene blue from aqueous solution by polyacrylamide grafted potato starch copolymers with a high natural polymer content

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Keywords: starch, starch copolymers, polyacrylamide copolymers, superabsorbent, methylene blue

Abstract: Polyacrylamide-g-starch copolymers with a high content of natural polymer from 60 to 90 wt.% and crosslinked potato starch were tested for removal of methylene blue from aqueous solutions. Starch superabsorbents were synthesized by free radical initiated polymerization using ammonium persulfate as initiator and N,N'-methylenebisacrylamide as crosslinking agent. The obtained materials were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, thermal analysis, X-Ray diffraction and laser scanning microscopy. The effect of polyacrylamide content in the starch graft copolymers, treatment time, dye concentration and pH of aqueous solutions on adsorption efficiency and swelling measurements were investigated. A sorption of dye by starch copolymers mechanism was proposed. The satisfactory results were assigned to the composition and structure of the synthesized copolymers.

109
Time-efficient technology for the production of biodegradable vascular stents using the micro-injection method

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Keywords: avscular stent, microinjection, biodegradable scaffold, biodegradable polymers

Cardiovascular diseases (CVDs) are the greatest cause of death for people all over the world. Biodegradable vascular stents have attracted much attention as an alternative to metallic stents, cause they pose as drug carrier, as well as mechanical support of the vessel until restoration and are completely degradable. Moreover, their application is not burdened with typical disadvantages resulting from the use of metal stents, such as vascular inflammation and thrombosis. The aim of the research was to develop technology for the production of vascular scaffolds by micro-injection and optimize their implantation process. The research consisted of synthesis and processing of material, laboratory tests and *in vivo* studies. As a result, stents with diameters of 3.0 mm (wall thickness 150 μm), 3.8, 5.4 and 7.4 mm (wall thickness 200 μm) were obtained, which were clamped on the catheter and successfully implanted according to the same procedure as for the implantation of commercially available stents.

Acknowledgement: *The research was carried out as part of project of The National Centre for Research and Development No. POIR.04.01.02-00-0105/17-00 "The technology for developing and obtaining the next generation of vascular stents through microinjection". Thanks to Keyence for providing a VHX-7000 digital microscope for imaging of the received stents and their quality control.*

110
Bioresorbable 3D printing filament for biomedical applications

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Keywords: 3D printing, biomedical grade filament, production, scaffold, poly(lactide-co-glycolide)

Currently, 3D printing has more and more applications. It is used both for engineering (rapid prototyping) as well as in the field of medicine and science. One of the simplest and most popular 3D printing method is Fused Deposition Modeling (FDM), based on the additive manufacturing by thermal processing of plastics. The market is full of various types of construction materials, but there is a lack of certified, biodegradable and biocompatible filaments that could be used for scientific purposes, e.g. in the production of cell scaffolds. In presented research, a poly(L-lactide-co-glycolide) copolyester in the form of 3D printing filament was developed and produced. Printing tests were carried out to prepare cell scaffolds for fibroblast culture. The influence of the infill configuration of the individual layers on the effectiveness of the colonization by fibroblasts was tested. Cells colonization depended on the size and shape of pores of the scaffold, which can be controlled by the 3D printing.

111
TOPEM®-DSC method for analysis of the network of liquid crystalline epoxy composition

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Keywords: liquid-crystalline epoxy resins, curing process, temperature-modulated DSC, thermosets

The conducted research aimed to determine the course of the cross-linking reaction of the liquid-crystalline epoxy composition. The mixture of the monomer MU22 with m-PDA diamine was examined by calorimetric analysis. The TOPEM®-DSC analysis method was used, which enables the separation of reversible and irreversible reactions. This technology gives the opportunity to obtain the simultaneous measurement of material properties as a function of temperature and time, in a wide frequency range, during only one measurement. ^{1}H-NMR spectra of the synthesized epoxy resin MU22 and diamine m-PDA were also recorded, for which all resonance signals corresponding to individual hydrogens in the molecule were identified.

112
Aminolysis of poly(ethylene terephthalate) as a method of waste management

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Keywords: recycling, aminolysis, PET

Aminolysis is one of the promising methods of chemical degradation of poly(ethylene terephthalate) (PET). This process is based on a direct reaction between an amine and PET (ester) often using catalysts. The products of this reaction are an symmetric diamides and ethynyl glycol. Currently conducted research is aimed at carrying out a waste-free aminolysis of recycled PET. In this respect, it is checked the possibility of using the obtained products in other important fields of technology, such as solar cells or as fuels additives. The results of these studies may allow for the development of effective methods of rPET management, what now currently is an important aspect due to its unlimited availability and low biodegradability.

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113
The relationship between the structure of polyolefin raw materials and the properties of waxes, products of their thermal degradation

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Keywords: polyolefines, polyolefine waxes, thermal degradation, structure, properties

Synthetic waxes are increasingly used in many industries. The main industrial process for the production of polyolefin waxes is the thermal degradation of various polyolefin raw materials. However, the comprehensive characterization of the process of thermal degradation of polyolefins to waxes is still insufficient. The aim of the work was to investigate the thermal degradation of polyolefins (HDPE, LDPE, LLDPE, EMAA), on a laboratory scale under various conditions, to polyolefin waxes. The results allowed to determine the impact of the raw material's structural features, including molecular weight and its distribution (GPC), the number and type of branches, and the share of unsaturation (FTIR) and the homogeneity of macromolecules (SSA) on similar structural elements and properties of the obtained polyolefin waxes.

114
Biodegradable, polylactide containing spherical and spheroidal particles: preparation, properties, degradation

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Keywords: biodegradable microspheres, poly(D,L-lactide-co-glycolide), prolate spheroidal particles, particles degradation

Literature reports devoted to preparation and biomedical applications biodegradable particles with shape different from spherical are very scarce. The aim of the studies is to compare spherical and spheroidal particles in regard to properties, biological membranes penetration and degradation in physiological conditions. The spheroidal particles composed of poly(D,L-lactide-co-glycolide, PGLA) were prepared from the spherical ones (D_n=3.2 µm, D_w/D_n=1.32) by uniaxial elongation of poly(vinyl alcohol) film with embedded microspheres in controlled conditions above T_g of polymers. Prolate spheroids with controlled aspect ratios (denoted as ratio of longer to shorter axis) in the range 2-8 were obtained. The results of studies revealed significant differences of PGLA microspheres and spheroids in terms of surface and internal composition, model membranes interactions and degradation time.

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115
Degradation studies of biopolymer welded joints

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Keywords: welding, welded joint, biopolymers, hydrolytic degradation, electrospray ionization mass spectrometry (ESI-MS^n)

The welding methods in many cases are very useful for the formation of advanced biomaterials from polymers. The impact of the welding process on the structure and properties of welded biopolymers and their ability to hydrolytic degradation has been studied. The samples were made from PLA and PHA polyesters, using different welding methods: ultrasonic and heated tool welding. The obtained results of hydrolytic degradation indicated that biopolymers welds started to degrade faster than unwelded parts of the samples. It was found that the hydrolysis of the PLA and PHA welds occurs by the random ester bond cleavage and leads to the formation of oligomers with the shorter chains, similarly as previously described for PLA and PHB.

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116
Biodegradation of surfactant-loaded polymer beads in soil and sea water

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Keywords: biodegradation, beads, sodium alginate, gellan gum, surfactant

The problems linked to plastic wastes have led to the development of biodegradable materials. External environmental factors, for example types and amount of microorganisms, temperature, UV exposure, pH, and water salinity influence the rate of biodegradation. Combination of the above conditions is characteristic of the selected environment such as water, compost, soil, and activated sludge. The study of the polymer materials decomposition in different environments allows to determine their biodegradability and changes occurring in the physicochemical properties of the materials.

The aim of my research was to prepare beads based on sodium alginate and gellan gum containing a surfactant by extrusion method and to assess the biodegradation of samples in sea water and soil. The biodegradation of the prepared beads was determined using a respirometric method with a WTW OXITOP—Control 110 set, which analyzed the microbial respiration activity (the oxygen uptake) over 28 days.

Acknowledgment: *Financial support from the National Science Centre (NCN, Krakow, Poland) Grant No 2018/31/N/ST8/02007 is gratefully acknowledged.*

117
Synthesis novel biodegradable aliphatic polyestersamines with functional pendant groups based on tartaric acid

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Keywords: polyester, polycondensation, ROP, functional polymer, biodegradable polymer

The presented research covers the multi-step synthesis and characteristics of the novel biodegradable and biocompa-tible aliphatic polyesteramines obtained based on tartaric acid and diethanolamine. Obtainment of innovative polymer materials involves several processes. The first step consisted of modification selected monomers by protection of reactive hydroxyl and amino groups. The effective protection of functional groups enabled the use of theses monomers in polycondesation and followed by polymerization ROP with lactides. Finally, poly L-lactide -co -tartarate butylene and poly (L -lactide - co - tartarate ethanolamine) with pendant reactive amino and hydroxyl groups was obtained. All the synthesis steps and reactions were controlled with NMR and FTIR measurement. These synthesized polymeric materials can have applications as special reactive matrix for cell's scaffolds and in drug controlled release.

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118
Ethylene-propylene-diene (EPDM) rubber composites filled with raw silicon carbide and its hybrid systems with conventional mineral fillers

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Keywords: silicon carbide, ethylene-propylene-diene rubber, elastomer composites, polymer composite properties, hybrid fillers

In the present work, the effect of silicon carbide (SiC) and its hybrid systems with different fillers (silica, carbon black, graphene, hydrotalcite, haloysite) on the rheometric measurements, crosslink density, mechanical performance, aging stability, morphology, thermal behaviour and flammability of the ethylene-propylene-diene (EPDM) rubber composites were discussed. It was found some technically promising synergetic effects of the hybrid filler systems used in the study on the EPDM composites performance. The most promising results have been obtained for HAL/SiC and LDH/SiC hybrid systems which compromised the high flame retardancy character of SiC with satisfactory mechanical performance of the final composite. The present study highlights the significant potential of silicon carbide and its hybrid systems as effective fillers improving the properties of elastomer composites.

119
Preparation and characterization of polyethylene composites with waste plant fillers

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Keywords: biocomposites, polyethylene, waste plant fillers, mechanical properties, rheology

The aim of the study was to obtain and characterize of polyethylene composites using various types waste plant fillers, i.e. maple, poplar and linden leaves as well as black and green tea grounds added to the polymer matrix in the amount of 10, 25 and 50 wt %. The influence of the type, amount, size and distribution of filler particles in the polymer matrix on the structural, thermal, rheological and strength properties as well as water absorption of the obtained composites was investigated. It was found that the tested plant waste can be successfully used as natural fillers of polyethylene composites, being a cheaper alternative to wood flour used in known wood-polymer materials. The use of such natural fillers reduces the consumption of petrochemical polymers and increases the susceptibility of these materials to biodegradation and/or biodeterioration, making them more environmentally friendly.

120
Polyurethane elastomers modified with polyhydroxybutyrate and graphene oxide

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Keywords: polyurethanes, polyhydroxybutyrate, graphene oxide, composites

Polyurethane (PUR) elastomers were synthesized by the prepolymer method. There was determined the influence of the presence of poly([R,S]-3-hydroxybutyrate) (R,S-PHB) in the structure of soft segments, as well as of graphene oxide (GO) in the matrix of the obtained composite, on the properties of polyurethane. Chemical modification of PUR with 30% wt. R,S-PHB influenced the interactions of PUR chains and its crystallinity. This lowered the mechanical properties of PUR and increased the hydrophilicity and water vapor permeability. On the other hand, blending PUR with 1.5% wt. GO, did not affect the structure, crystallinity and hydrophilicity of the polymer, but increased its mechanical properties and decreased water vapor permeability. Thus, by selecting an appropriate modifier, the properties of the elastomers can be influenced.

121
Biocomposites of chokeberry pomace grafted by lactic acid oligomers

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Keywords: lignocellulosic material, chemical modification, poly(lactic acid) composites, in situ polymerization, grafting biocomposites, biodegradable composites

Chokeberry pomace (CP), which is waste from the food industry, has been chemically modified with lactic acid (LAc). As a result of the direct condensation of LAc, lactic acid oligomers (OLAs) were grafted onto lignocellulosic filler. The modification aims to reduce the hydrophilicity of the natural filler and improve the adhesion to the hydrophobic polymer matrix. Additionally, free OLAs synthesized during condensation can act as a natural plasticizer. The manufactured PLA-based composites were characterized by higher tensile strength than those with unmodified filler. DSC and DMA analysis showed a significant reduction in the glass transition temperature compared to neat PLA, which confirms the plasticizing effect of OLAs. The results are promising, and can contribute to increasing the use of agri-food lignocellulosic residue in manufacturing biodegradable packaging.

122
Low density polyethylene composites filled with carbon nanotubes/iron (III) oxide hybrid nanoparticles

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Keywords: carbon nanotubes, graphene/iron oxide hybrids, polyethylene composites, crystallinity degree, thermal, electrical properties

The aim of this work was to characterize the structure and basic properties of multifunctional LDPE composites with a hybrid filler based on multi-walled carbon nanotubes (MWCNTs) coated with iron (III) oxide nanoparticles. (IO NPs). The filler structure was determine by X-ray diffraction (XRD), Raman spectroscopy and scanning and transmission electron microscopes (SEM-EDS, TEM). LDPE composites with random and partially arranged distribution of filler NPs were prepared. Partial order of filler NPs in LDPE matrix was obtained using external magnetic field, as was confirmed by increased area ratio of D band to G band in Raman spectra of graphene layers. XRD and differential scanning calorimetry (DSC) were used to determine the effect of MWCNTs/IO NPs content and ordering in magnetic field on the crystallinity degree of LDPE matrix. The crystallization degree clearly increased for 5 vol.% and continued to rise up for 10 vol.% of filler loading applied in magnetic field. The role of magnetic treatment on thermal and electrical properties of LDPE-MWCNT/IO composites was also studied to the possibility of application them as thermally and electrically conductive polymer composites.

123
Melt rheology of polylactide and its blends with thermoplastic starch

Justyna Ostrowska, Karolina Sołtan, Waldemar Sadurski, Piotr Tyński, Magdalena Paluch

The Łukasiewicz Research Network – New Chemical Syntheses Institute, Puławy, Poland

Keywords: polylactide (PLA), thermoplastic starch (TPS), rheology, capillary rheometer, extrusion

Rheological studies of polymer melts are widely used to support the processing of biodegradable polymers. Rheological measurements provide information on the behavior of polymers in the melt, viscoelasticity, elongation and shear, therefore they are necessary to control and determine further directions of plastics processing.

This report presents the results of the rheological measurements of PLA/TPS blends in comparison to neat polymers. The PLA/TPS blends were prepared in various weight proportions by using twin-screw extrusion. Melt rheological properties of the granulates were studied using a capillary rheometer and plastometer. The effects of share rate, temperature and TPS content on the true viscosity of the blends were described. Generally PLA/TPS blends exhibited a pseudoplastic flow behavior where the viscosity decreased with increasing shear rate and temperature.

124
Investigation of the properties of different types of elastomers for medical applications with added chitosan

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Keywords: chitosan, silicones, elastomers, antimicrobial

Tests have been conducted with selected elastomers for medical applications with the addition of chitosan. Chitosan, a non-toxic natural polymer has an established antibacterial and anti-inflammatory effect. Due to its properties, it can be used as an antimicrobial agent against bacteria, fungi and viruses. Composites (silicones, nitrile rubbers, natural rubber and EPDM) for medical applications with the addition of chitosan were prepared and the antibacterial, physico-mechanical properties, and the dispersion by SEM (Scanning Electron Microscope) of the composite thus produced were studied. Of the samples tested, three were selected having very good antibacterial properties for Escherichia coli (ATCC 8739) i Staphyloccocus ureus (ATCC 6538P), according to ISO 22196:2011, and very good chitosan dispersion and good physico-mechanical properties. These results are the subject of a patent application P.436706.

125
Processing of thermoplastic starch/polylactide blends

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Łukasiewicz Research Network – New Chemical Syntheses Institute, Puławy, Poland

Keywords: thermoplastic starch, biodegradable polymers

Thermoplastic starch (TPS) is a natural hydrophilic material which is used for the preparation of biodegradable plastics. The application of TPS is limited due to unsatisfactory mechanical properties, poor resistance to moisture as well as degradation. To overcome these disadvantages, thermoplastic starch is mixed with other polymers and additives to improve mechanical and thermal properties. Blending thermoplastic starch with polylactide leads to cost-effective biodegradable materials which can be processed by various methods used in the processing of thermoplastics.

The paper presents the results of research on obtaining and processing TPS/PLA blends. Biodegradable blends were prepared in the extrusion process, and then processed by various techniques. The blown film extrusion and cast film extrusion process were used to prepare biodegradable films while injection technique was used to obtain moldings.

126
Polyester resin composites reinforced with CFRP recyclate in sliding materials, as a method of mechanical recycling

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Keywords: CFRP waste, composites, sliding materials, mechanical recycling, tribology

CFRP waste is a difficult material to recycle. Due to the presence of expensive carbon fibers, the interest in recycling is high. The current state of knowledge on the recovery of carbon fiber from composites is constantly expanding into new areas of use. The paper presents an attempt to use CFRP recyclates (rCFRP) as fillers in the production of sliding materials with the use of unsaturated polyester resin. The procedure of CFRP filler preparation in a multi-stage mechanical recycling process is described. The obtained composite with 10% by weight addition of rCFRP filler (in different particle size fractions) was tested for technological, mechanical and tribological properties. The obtained results allowed to conclude that CFRP recyclate improves the sliding properties of the resin, and the most favorable tribological and mechanical properties are shown by composites with rCFRP fractions of various sizes.

127
Surface properties of lignite as fillers for thermoplastic polymers

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Keywords: polypropylene, lignite, composites, surface free energy

The material features during the production of composites systems include surface properties. The hydrophilic or hydrophobic nature of the surface of the composite material can be assessed by measuring the contact angle. In the conducted tests, this parameter allowed for the assessment of changes in the hydrophobicity of the composite filled with various lignite fractions in comparison to the already described composites systems and the polymer matrix. The surface properties of the filler translate directly into the mechanical and functional properties of the composite.

128
Polymer blends of poly(3-hydroxybutyrate) and aliphatic polyurethanes based on hexamethylene diisocyanate and polyethylene glycols

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Keywords: aliphatic polyester, linear aliphatic polyurethanes, biopolymer, composites, thermal stability

Poly(3-hydroxybutyrate acid) (P3HB) is biocompatible biopolymer, and shows no cytotoxicity and mutagenicity. P3HB undergoes degradation to 3-hydroxybutyric acid and this is a natural metabolite in the human body. Therefore P3HB could be used as material of bioimplants and replace the synthetic, hard-to-degradable polymers. However, P3HB is a brittle material with limited thermal stability.

Therefore, in order to improve its mechanical properties and processing parameters by separating its melting point and degradation temperature, P3HB blends can be produced using, for example, linear aliphatic polyurethanes as modifiers. In work, linear aliphatic polyurethanes based on hexamethylene diisocyanate and polyethylene glycols were used. Addition of polyurethane obtained by the reaction of 1,6-hexamethylene diisocyanate and polyethylene glycol with a molecular weight of 400 g/mol (PU400) improved of the processing property parameters of P3HB and mechanical properties in the best way.

129
Application of layered anionic and cationic nanoclays intercalated with amino acids for modification of polymers and coatings

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Keywords: layered nanoclays, hydrotalcites, amino acids, polymers, coatings

Layered minerals including aluminosilicates and double hydroxides (hydrotalcites) attract considerable interest as catalysts, functional nanofillers for polymers and carriers for biologically active compounds. In our studies, montmorillonite intercalated with protonated amino acids, as well as zinc-aluminium and magnesium-aluminium hydrotalcites modified with anionic forms of amino acids, were prepared.

The obtained organically modified clays were used as in-situ additives in the synthesis of polyester resins and polystyrene as well as in the preparation of polyurethane and acrylic coatings. Advantageous effects of nanoclays on various properties of the modified polymers and coatings, including reduced flammability and improved surface, mechanical and antimicrobial properties were observed.

130
Phytochemical studies and evaluation of the antioxidant activity of extracts prepared from different plants and extraction solvents

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Faculty of Chemistry, Nicolaus Copernicus University, Toruń, Poland

Keywords: plant extracts, polyphenols, flavonoids, antioxidant activity

Plant extract is a complex mixture of compounds that can have beneficial effects on the skin, including regenerating, soothing, antioxidant and anti-inflammatory properties. The research aimed to obtain extracts from the following polish herbs: wild pansy (*Viola tricolor*), heath speedwell (*Veronica officinalis*), ground-ivy (*Glechoma hederacea*), ribwort plantain (*Plantago lanceolata*); flowers: yarrow (*Achillea millefolium*), elderberry (*Sambucus nigra*), small-leaved lime (*Tilia cordata*); rhizome: tormentil (*Potentilla erecta*). Extracts were prepared using the Soxhlet apparatus with water and ethanol as solvents. They were characterized by the content of polyphenols, flavonoids and antioxidant capacity (CUPRAC and FRAP) and compared by the used solvent for extraction and type of plant.

Acknowledgments: *Financial support from Grants4NCUStudents research project under the "Excellence Initiative – Research University" programme is gratefully acknowledged.*

131
Estimation of the composition gradient during simulation of copolymerization

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Keywords: gradient polymers, Monte Carlo simulations, statistical analysis

A basic statistical analysis of the resulting data obtained in simulations in copolymerization of two bifunctional comonomers was conducted. To obtain data for statistical processing, a simple program to study a terminal model of copolymerization was implemented using Monte Carlo techniques. The program also allowed for the addition of consecutive portions of monomers during the simulation.

The gradient of the copolymers was determined by averaging the composition of successive segments arranged along the chains of macromolecules over the entire reaction system.

It was found that the applied method allows one to estimate the shape of the product gradient after simulating relatively small reaction systems.

132
Understanding poly(carbonate-urea-urethane)s synthesis using Monte Carlo simulations

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Keywords: Monte Carlo simulations, shape-memory polymers, poly(carbonate-urea-urethane)s, dynamic Lattice Liquid model

Shape memory polymers are characterized by the ability to change shape under an external impulse. This materials are usually segmented, where the elastic segments they contain are in an amorphous form. This segments are enabling the stretching of the polymer bundles and the fixation of the temporary shape and the impulse return to the basic shape. Rigid segments are the cross-linking points responsible for the durability of the basic shape.

Monte Carlo simulations were employed for better understanding the process of preparation of poly(carbonate-urethane-urea) elastomers. The computational experiments were used to simulate of the process of two-step synthesis of oligocarbonate diols, followed by the process in which the prepolymer, as well as its curing with water vapor.

133
Stereological-fractal analysis as a tool for a precise description of the polymer morphology

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Keywords: polymer morphology, structure-properties relationships, stereological analysis, fractal analysis

A precise quantitative description of the morphology of a polymeric material is crucial to establish relation between the properties and structure of the material. Novel morphological analysis tools should be quantitative techniques, which would yield objective and reproducible values for any morphological structure and enable statistically proven comparisons. These requirements are met by the stereological-fractal analysis (SFA). This method bases on the fractal dimension, the generalized fractal dimension, lacunarity and the shape descriptors like elongation factor, Surface factor, irregularity parameter and bulkiness. The SFA method combines three various tools that were previously used separately. Therefore, this method makes it possible to describe more precisely and accurately the unique features of the investigated structure. This work presents both the theoretical fundamentals of SFA and the results of such an analysis for selected polymeric materials.

134
Novel stabilizers for lyotropic liquid crystalline nanoparticles studied by cryo-TEM and XRD

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The investigation of properties of amphiphilic block copolymers, as stabilizers for non-lamellar lyotropic liquid crystalline nanoparticles (LLCNPs), represents a fundamental issue for the formation, stability and upgraded functionality of these nanosystems.

In this work the formulations of aggregated structures of glyceryl monooleate (GMO) and linear block copolymers: poly(ethylene oxide)-*b*-poly(lactic acid) and poly(ethylene oxide)-*b*-poly(5-methyl-5-ethyloxycarbonyl-1,3-dioxan-2-one) were prepared by Top Down Method (TD). The morphology of particles was studied by cryogenic transmission electron microscopy (cryo-TEM), fast fourier transform (FFT) and X-ray diffraction (XRD). The copolymers served as stabilizers of LLCNP structures. This study allows to establish the influence of hydrophobic block present in copolymers chains on morphology and internal organization of LLCNPs and broaden the toolbox of polymeric stabilizers.

135
The effect of multiple processing on the thermoplastic starch properties

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Łukasiewicz Research Network – New Chemical Syntheses Institute, Puławy, Poland

Keywords: thermoplastic starch (TPS), multiple processing, extrusion

Starch is a natural biopolymer obtained from renewable raw material which found application in industrial packaging. Starch can be converted into thermoplastic material by extrusion process, which is simple method to produce films using conventional equipment applied in plastic industry.

This paper presents the results of multiple processing on the thermoplastic starch properties. Plasticization of starch was conducted in a twin screw extruder in the presence of a plasticizer. The thermoplastic starch (TPS) granulate was processed three times in extrusion process. TPS pellets obtained at each stage were characterized by GPC, TG, DSC methods. The Karl Fisher method was used to examined water content in granulates.

136
Poly(phenylene sulphide) –polymer with unique properties, innovative production technology

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Keywords: PPS, engineering polymer, production technology

Poly(1,4-phenylene sulfide), which is commonly called PPS belongs to the group of engineering polymers. This polymer is characterized by high abrasion resistance, dimensional stability in an aggressive chemical environment and thermal resistance. Poly(phenylene sulphide) was syn- thesized on a laboratory and large-scale laboratory scale, the obtained polymer was purified and dried, and then in the process of extrusion and injection to obtain material for mechanical and electrical tests. Using the obtained results, a process simulation model was developed us- ing computer techniques, as well as engineering and design work leading to the base project. The research was carried out as part of a project co-financed by the Intelligent Development Operational Program 01.02.00-00-0040 / 17 by the consortium: Grupa Azoty "Siarkopol" S. A., Grupa Azoty PKCh sp. z o.o. and Łukasiewicz – ICSO "Blachownia".

137

Development of new experimental methods based on pulse radiolysis for studying kinetics and mechanism of fast reactions in polymer systems

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Keywords: reaction kinetics, rate constants, free radicals, polymerization, pulse radiolysis

Precise synthesis of macromolecules and polymer-based materials requires the underlying mechanisms and kinetics to be known in detail. At IARC two new experimental methods are being developed, aimed at providing tools to study fast processes in polymer systems. PR-MALLS is a system where nano- and microsecond pulse radiolysis is used for momentary generation of precisely known concentration of free radicals, followed by real-time observation of changes in molecular weight and radius of gyration by multiangle laser light scattering. PEP-SEC is a system alternative to the well-established PLP-SEC, where polymerization and termination is induced by electron pulses instead of laser pulses. PEP-SEC eliminates the use of photoinitiators and allows to follow polymerization in non-transparent and confined spaces. Fully operational model systems have been built, which currently undergo testing and optimization.

Author index

Keywords

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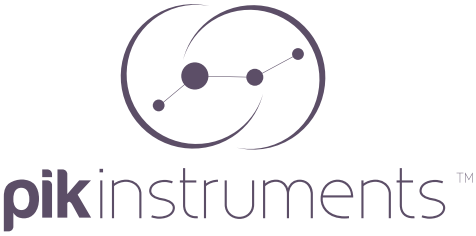

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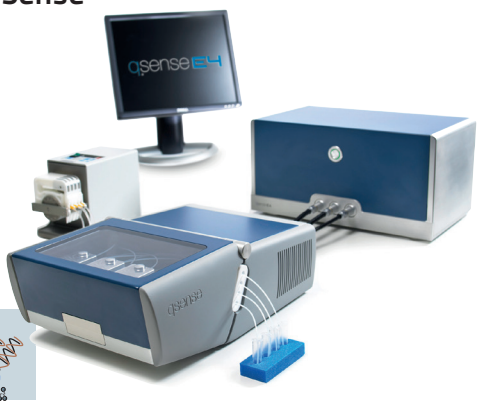

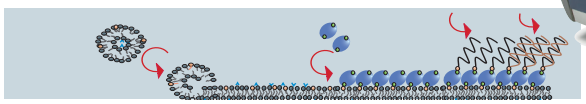

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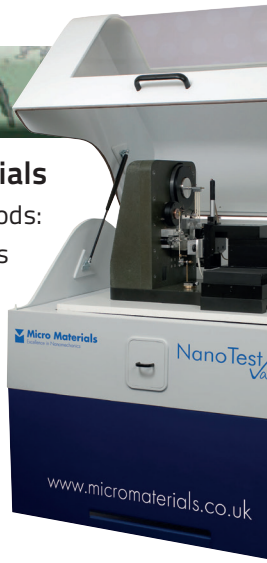

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