KAUNAS UNIVERSITY OF TECHNOLOGY
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Baltic Polymer Symposium 2016

KLAIPEDA
September 21-24, 2016

PROGRAMME AND ABSTRACTS

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BALTIC POLYMER SYMPOSIUM 2016

AGENDA

	September 21, 2016
17.00 – 19.00	**Arrival and Registration -** *Hotel "Amberton Klaipėda" (Naujojo Sodo str. 1)*
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LIGHT-EMITTING MACROMOLECULES FOR PHOTONIC APPLICATIONS

P.J. Skabara

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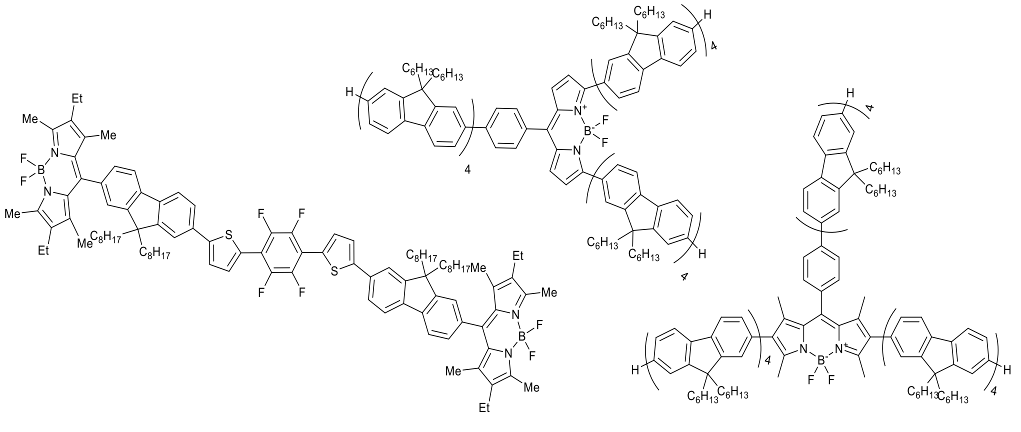
Materials suitable as active components in organic light-emitting diodes (OLEDs) have attracted widespread interest in recent years, as this technology develops towards replacing existing less efficient technologies, e.g., incandescent and fluorescent bulbs, in consumer applications such as solid-state lighting. To this end, both polymers and molecular structures have been exploited. While polymers offer high luminescence and solubility, they can suffer from problems associated with high polydispersity and batch-to-batch reproducibility. Molecular or oligomeric systems offer advantages such as monodispersity, synthetic reproducibility and, depending on structure and device fabrication requirements, they can be processed via vacuum deposition or solution processing techniques.

Devices emitting white light with higher efficiencies than traditional light bulbs are much sought after. Significant improvements have come through the development of inorganic white light emitting diodes (LEDs) based on gallium nitride and organic versions employing polymers, macromolecules or molecules. This presentation describes a hybrid approach, combining yellow-emitting organic materials with a blue-emitting inorganic LED. This approach couples very efficient blue emission with the flexibility, fast modulation speed and cost effectiveness of the organic colour converter. For the organic converter molecule BODIPY is used as the emitter, and linked to a complex absorbing unit designed to efficiently absorb a suitable fraction of the blue light. The combined linear fluorene-containing-BODIPY compound can be adapted to control the quality and properties of the white light and we show how it can be easily combined with industrial-grade blue LEDs. Applications of the resulting devices are presented and include white-light LEDs and visible light communications (Li-Fi).



ANTI-ICING AND DE-ICING SURFACES

P.M. Claesson[1,2], G. Heydari[1], C. Visnevskij[3], R. Makuska[3], E. Tyrode[1]

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Ice accumulation is a severe problem in cold climates, where it affects outdoor structures and infrastructures, as well as human life. It can result in critical performance problems and safety concerns for instance in road, air and sea transportation, transmission lines, marine and offshore structures, wind turbines and heat exchangers. Present active ice-combating approaches possess environmental, efficiency and cost drawbacks. Thus, fabricating icephobic surfaces or coatings impeding ice formation (anti-icing), but facilitating ice removal (de-icing) is desired. However, different conditions of the ice propagation environment add to the complexity of the problem. An icephobic surface that works for a certain application might not be a good candidate for another.

In this presentation we will discuss two approaches for achieving passive anti-icing and de-icing properties. The first one relies on the water repellency of superhydrophobic surfaces to also achieve iceophobic surfaces. Such surfaces have shown great promise in laboratory experiments under low humidity conditions. However, we mean that such surfaces will not have significant iceophobic properties under realistic conditions, which we attribute to condensation and frost formation that promote wetting.[1, 2]

An alternative approach is to utilize the subzero freezing point of hydration water next to hydrophilic polymers or surfaces to achieve a thin water layer on which ice easily can slide. To this end we have measured the ice adhesion strength on hydrophilic and molecularly smooth mica surface down to – 35°C. Indeed, record low ice adhesion strength was found suggesting that the use of hydration water that freezes at sub-zero temperatures could be a rational approach to reduce ice adhesion. To achieve similar results on real rough surfaces requires formation of thicker hydration layers. We have recently shown that promising results can be achieved using electrostatically anchored brush polymers of poly(ethylene oxide).[3]

References

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3. G. Heydari, E. Tyrode, C. Visnevskij, R. Makuska and P. M. Claesson, *Langmuir*, 2016, **32**, 4194-4202.

ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL INVESTIGATIONS AS A WAY TO EVALUATION OF ORGANIC COMPOUNDS IN TERMS OF (OPTO)ELECTRONICS APPLICATIONS

M. Lapkowski[1,2], S. Pluczyk[1], P. Zassowski[1], L. Galmiche[3], P. Audebert[3], R. Rybakiewicz[4], M. Zagorska[4], A. Pron[4]

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Electrochemistry is a widespread scientific discipline which provides lots of informations about redox properties, stability, the conversion and storage of energy, *etc*. It also allows to determine the electron affinity and ionization energy of investigated compounds the values of which are correlated with energies of HOMO and LUMO- crucial parameters for (opto)electronics applications. Spectroelectrochemistry- the combination of electrochemical methods with spectroscopy, makes possible to characterize species which are formed as intermediates or as products in redox processes. Moreover, it is helpful in elucidation mechanism of electrode reactions.[1,2]

In this work we present examples of electrochemical and spectroelectrochemical investigations of organic compounds such as *s*-tetrazine or arylene diimide derivatives. The characterizations of studied compounds were performed using: electrochemical techniques including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements; spectroelectrochemical investigations such as UV-Vis, EPR and Raman spectroelectrochemistry.

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Donor-Acceptor Light Emitting
EXCIplexes as Materials for Easy-to-Tailor Ultra-efficient OLED LIGHTing
H2020-MSCA-ITN-2015/ 674990

AMBIPOLAR ORGANIC SEMICONDUCTING COMPOSITES

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Organic semiconductors able to transport both holes and electrons are highly demanded for several applications in organic electronics, e.g. for constructing complementary circuits or light-emitting transistors. Active semiconducting layers in such devices should exhibit high and balanced mobility of holes and electrons. One should take into account also, that the printed organic electronic technology requires solution processable materials.

In this work we present two solution-based methods allowing to produce ambipolar semiconducting composites made of mixtures of *p*- and *n*-type semiconductors (low molecular weight materials or polymers). Crucial problem to be solved in such composites is continuity of both *p*- and *n*-type phases. The elaborated by us methods employ a tendency of organic semiconductors for self-organization, leading to formation of continuous transporting paths for holes and electrons. We demonstrate that the transistors made of such composites exhibit high hole and electron mobility and symmetrical characteristics.

Acknowledgements

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POLARIZATION EVOKEN PECULARITIES IN ULTRAFAST LASER 3D NANOLITHOGRAPHY

M. Malinauskas, S. Rekštytė, D. Gailevičius, L. Jonušauskas, R. Gadonas

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A systematic study of light polarization induced effects in direct write femtosecond laser 3D lithography is presented [1]. It is demonstrated that coupling between linear polarization of the writing light electric field can be implemented to fine-tune feature sizes in structuring of photoresists at a nanoscale. The vectorial Debye focusing is used to simulate polarization effects and a controlled variation up to ~20% in the line width is shown experimentally (Fig. 1) for the identical axial extent of the polymerized features [2]. The revealed dependencies are relevant for a light-matter interaction at tight focusing in laser 3D nanolithography applying it for structuring of photonic and optical components [3]. It is supposed that the polarization orientation's influence will be significantly enhanced in conductive particle doped polymers which is an emerging field in state-of-the-art 3D printing based plasmonic and electric circuit micro-/nano-manufacturing [4,5].

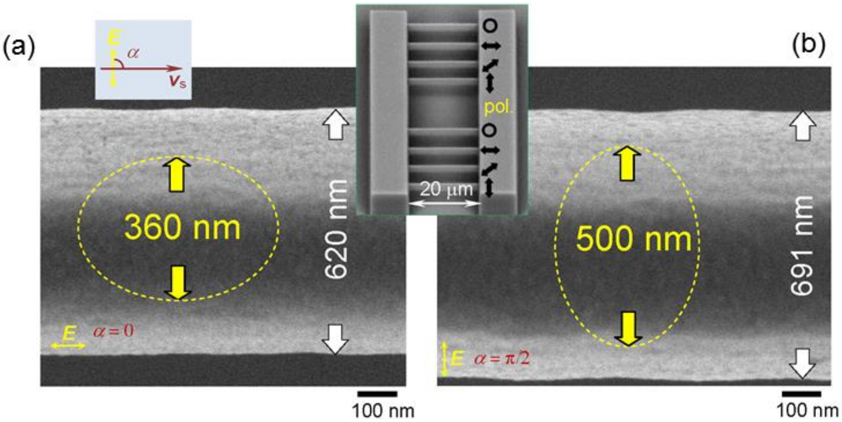

Fig. 1. Top-view SEM images of 3D suspended bridges out of SZ2080 with 1% BIS photo-initiator at the same conditions (scanned along the X-axis at velocity v_s) except for light polarization direction: $\mathbf{E}\parallel\mathbf{v}_s$ (or angle $\alpha=0^\circ$) and $\mathbf{E}\perp\mathbf{v}_s$ (or angle $\alpha=90^\circ$). The width difference is 10.3% for NA = 1.4 and λ = 1030 nm. The ovals show the FWHM intensity cross section calculated by vectorial Debye formula $W_l \times W_s \equiv$ 500×360 nm (see [1] for details). The inset shows a typical object used for determination of the height of the structures.

Acknowledgements

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SYNTHESIS OF STAR-SHAPED (CO)POLYMERS FOR PREPARATION OF BIODEGRADABLE SCAFFOLDS FOR BONE REGENERATION

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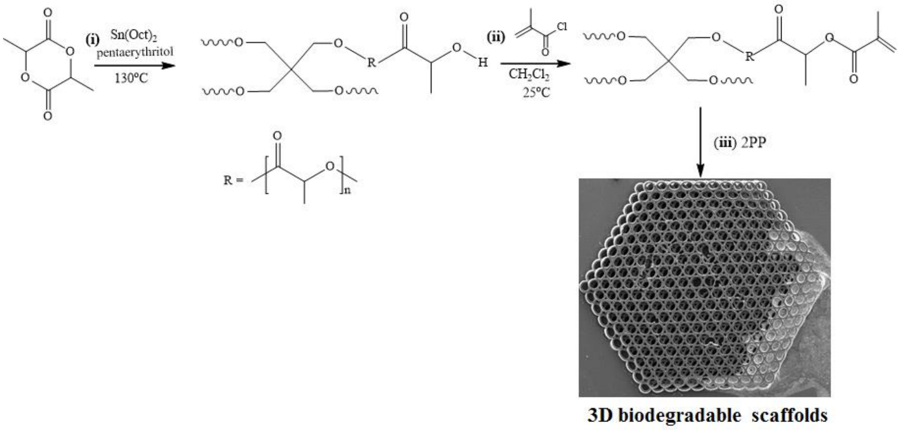
In this work, the strategy for the synthesis of methacrylate-terminated star-shaped poly(D,L-lactide) (SSL) and preparation of biodegradable 3D scaffolds from these polymers will be presented. This strategy consists of $Sn(Oct)_2$- or TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene)- catalyzed bulk ring-opening polymerization of D,L-lactide using pentaerythritol as tetrafunctional initiator followed by end-capping of resulting star-shaped poly(D,L-lactide) with methacryloyl chloride (see Scheme 1).[1] The influence of the catalyst nature and monomer to initiator ratio on the resulting polymers properties will be discussed here. Basically, the bioresorbable star-shaped polymers were obtained in high yield (>90%) and were characterized by low molecular weight (M_n~2,000–4500 g mol^{-1}), which can be easily adjusted by the monomer to initiator ratio, and quite narrow MWD (M_w/M_n<1.2).



Scheme 1. Synthetic strategy for the preparation of star-shaped polylactides and 3D scaffolds therefrom using method of two-photon polymerization (2PP).

Finally, biodegradable scaffolds with a 3D microscopic architecture have been fabricated from a novel SSL by applying the 2PP technique (Scheme 1). It has been demonstrated that the fabricated SSL scaffolds are able to provide a beneficial microenvironment for the osteogenic differentiation of mesenchymal stem cells *in vitro* and support *de novo* bone formation *in vivo*, which shows them as very promising 3D microstructured implants for bone regeneration applications.[1]

Acknowledgements
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LUBRICATION SYNERGY OF PHOSPHOLIPID – POLYMER MIXTURES

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Phospholipids and hyaluronan are important in synovial joint lubrication. It has been shown that while phospholipids alone provide superior lubrication hyaluronan is easily expelled from the surfaces. Why Nature add a seemingly unnecessary component to a complex lubricating blend? Is there any synergy and what kind of synergy is there between phospholidpids and hyaluronan in lubrication?

It has been shown by small angle X-ray scattering that hyaluronan associates with the outer shell of DPPC vesicles in bulk solution. Since both components are present in the synovial fluid they should form self-assembly structures. In this work, we follow the adsorption from a mixed hyaluronan/DPPC solution by QCM-D and conclude that significant adsorption occurs on silica surface. AFM imaging showes the adsorbed layer structure, which consists of a non-homogeneous phospholipid bilayer on top of which hyaluronan/DPPC aggregates are found. The presence of these aggregates generates a long-range repulsive force between surfaces. However, the aggregates are easily compressed and possibly removed from between the surfaces. A very low friction coefficient (< 0.01) and high load bearing capacity (≈ 23 MPa) are offered by the layers formed by adsorption from the mixed hyaluronan/DPPC solution. The presence of surface bound DPPC/hyaluronan aggregates provides a means for accumulation of DPPC lubricants on the sliding surfaces and thereby the presence of hyaluronan is synergistic.

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ENHANCEMENT OF LIGHT EMISSION USING ORGANIC FLUOROPHORES AS ANTENNAS IN UNUSUAL SITUATIONS: THE CASES OF TETRAZINES AND 2-D HYBRID PEROVSKITES

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Energy transfer between two fluorophores is a process which has been known for a very long time. However, in the standard case, its interest is limited, since while the absorption of the "antenna" fluorophore captures the light at an interesting wavelength, on the other hand, the part of the spectrum corresponding to the absroption fo the emmitter is usually lost.

On the other hand, the phenomenon has been used for fluorophores eeactivation, controlled deactivation with photochromes, and so on… A specially interesting case s when a good absorber is coupled with a good emitter, but possessing on the other hand a very weak absorption. This is the widely investigated case of lanthanide complexes, whose luminescence is based on high spin states f-f transitions extremely weakly absorbing, allowing the existence of luminophores with a very large Stokes shift.

A rarer case, almost unregarded, consists in the situation of a fluorophore, or a phosphor, havng a quite low absorption on the transition responsible for its fluorescence/phosphorescence. This is the case of tetrazine fluorophores, which fluoresce on a low-absorbance n-p* transition, and perovskites, where a weakly absorbing polariton delocalized state is responsible for light emission.

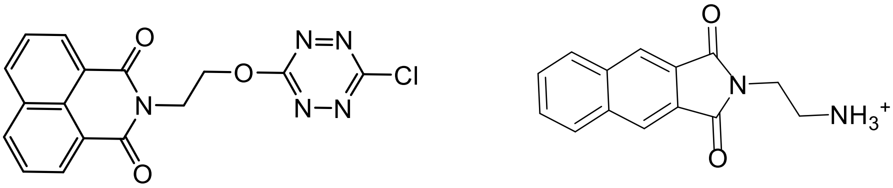

Fig. 1. Tetrazine activated by a 1,8-naphtalimide; 2,3-naphtalimide ammonium for a perovskite activation.

We have developped two specific chromophore antennas, featuring both a strong absorption, but also which are able to transfer very efficiently energy to both tetrazines[1] and selected 2-D perovskites[2] These are the imides presented hereabove. In the particular case of the perovskites, the challenge is not trivial, since only the energy transfer should occur, not being concurrenced by the electron transfer, and in addition, the cristallographic structure of te perovskite should be retained. The results will be discussed in the presentation, along with the oppurtunities opend by this approach.

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NEW HEAVY METAL COMPLEXES IN POLYMER MATRIX AS ACTIVE LAYER OF ORGANIC LIGHT EMITTING DIODE

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Within the past decade, organo - transition metal compounds have been attracting attention as an emissive material with possible application in electroluminescent devices such as organic light emitting diodes (OLEDs). Such kind of complexes can exhibit efficient emission from triplet states (phosphorescence) so, according to spin statistic, can increase the efficiency of electroluminescence.

The subject of this work were new heavy metal -Ir (III) complexes tested as light emitting dopants incorporated in polymeric matrix. Guest/host-type single layer light emitting diodes were fabricated from the most luminescent compounds, molecularly dispersed (1 wt%) in a matrix consisting of 70 wt% poly(Nvinylcarbazole) and 30 wt% 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole. Appropriate alignment of the matrix components energy levels and those of the studied compounds (Fig 1.) resulted in effective electroluminescence of the guest molecules.

One of the possible mechanisms of the photo- and electroluminescence generation in the guest/host configuration is the Förster energy transfer from the host matrix to the guest molecules. The efficiency of this processes was studied by photo and electroluminescence experiments carried out for layers of PVK + PBD with Ir(III) complexes.

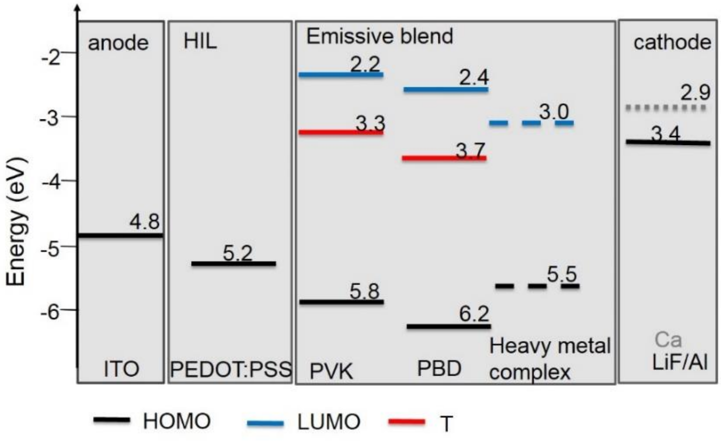

Fig. 1. Geometry of fabricated OLEDs.

Acknowledgements

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TAILORED THERMOSETS BY SEQUENTIAL DUAL CURING BASED ON CLICK REACTIONS

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Dual curing is a processing methodology based in the combination of two different and compatible polymerization reactions taking place simultaneously or sequentially in a well-controlled manner. Sequential dual curing processing allows to obtain stable materials after the first curing stage that maintain the ability, after application of a second stimulus, to activate the second curing stage and complete the process, leading to a fully-cured material with the desired final properties. This curing approach makes possible to obtain uncommon-shaped final materials such as spring- or bent-shaped thermosets with optimal mechanical and even shape-memory properties.

Click reactions are efficient, simple, selective and can be performed under environmentally-friendly conditions.[1] Their use is very advisable in sequential dual curing processing, since the control of both processes is quite easy and based in their chemistry and in the formulation of the reactive mixture. The tailoring of intermediate and final materials can be performed by selection of the proper formulation. The materials obtained after the first curing stage can be gelled or ungelled and loosely or tightly crosslinked at the end of the second curing stage.

Dual curing methodologies are classically performed in two stages, being one of them photoinitiated and the other triggered by heat. As an example of this methodology a sequential thiol-ene/thiol-epoxy dual curing will be presented and discussed.[2]

Alternatively, to reach new dual curing methodologies the use of off-stoichiometric formulations has been reported. The first stage process is a self-limiting click reaction between two multifunctional monomers with an excess of one of the two monomers. The second stage reaction is the thermally or UV-induced homopolymerization of the excess of unreacted groups. By selecting the structure of the monomers and the stoichiometry of the formulations, mechanical and thermal characteristics of the intermediate and final materials can be tuned. As an example of the combination of two thermal processes, a sequential curing of off-stoichiometric thiol-epoxy formulations with excess of epoxide will be explained.[3] The combination of a self-limiting aza-Michael addition at room temperature followed by the photopolymerization of the acrylate in excess constitute another dual methodology which, in addition, has the advantage to overcome the intrinsic oxygen inhibition of acrylate free radical homopolymerization.[4]

Acknowledgements

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CROSSLINKABLE HOLE TRANSPORT POLYMER ENHANCED CANDLELIGHT OLED WITH PRINTING FEASIBILITY

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Candlelight is currently the most human-eyes and physiologically friendly illumination source with high visual quality. With the employment of multiple candlelight complementary organic emitters, we have been able to generate lights mimicking that of candles. Earlier reported dry-processed candlelight organic light emitting diodes (OLEDs) exhibited high efficiency with more than 80% resemblance in the luminance spectrum to that of candle.[1-2] However, dry-process is not a favorable approach because of much material consumption. With the incorporation of a cross-linkable hole-transporting polymer, we can fabricate high-efficiency candlelight OLED via wet-process. The cross-linkable hole-transporting polymer, 3,6-bis(4-vinylphenyl)-9-ethylcarbazole (VPEC)[3] shows a high hole mobility of 1×10^{-4} cm^2 V^{-1} s^{-1} and a high triplet energy of 2.88 eV, favoring respectively the injection of holes into the emission layer and the confinement of triplet excitons generated therein to realize high efficiency. The resultant device shows at 100 cd m^{-2} for example an efficacy of 23.4 lm W^{-1}, an external quantum efficiency of 14.7%, a color temperature of 1,500 K, and a spectrum resemblance index (SRI) of 85. The high efficiencies of the device may also be attributed to the high lowest unoccupied molecular orbital of the VPEC layer that prevents overflow of the electrons from the emissive layer.

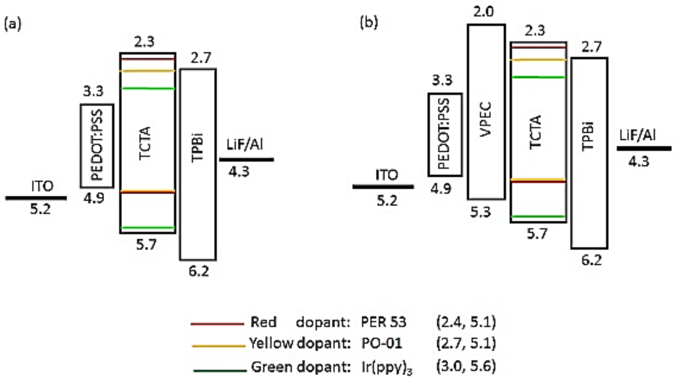

Fig. 1. Schematic illustration of the wet-processed candlelight OLEDs (a) without and (b) with a cross-linkable hole transporting material, 3,6-bis(4-vinylphenyl)-9-ethylcarbazole (VPEC).

Acknowledgements

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AROMATIC-FUSED DIKETOPHOSPHANYL COMPOUNDS: NEW ENTRIES TO PHOSPHORUS-CONTAINING π-CONJUGATED FUNCTIONAL MATERIALS

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Recently, π-conjugated organic compounds have been emerging as promising candidates for the organic optoelectronic materials. From the viewpoint of tailoring the functions, the incorporation of heteroatoms (e.g., N, Si, B, S, etc.) into carbon-based π-conjugated main-frameworks or peripherals is a promising and powerful strategy, allowing the significant electronic- and/or structural perturbations in the newly built conjugated systems. In this context, π-conjugated organophosphorus compounds, which contain a heavier congener of nitrogen, have attracted much attention as unique and promising scaffolds for functional π-conjugated materials.[1] Therefore, the development of new entries to organophosphorus π-conjugated scaffolds would provide us tremendous opportunities for the creation of new functional materials based on their unique properties. As a program of developing new organophosphorus scaffolds, we designed aromatic-fused diketophosphanyl compounds (Fig. 1). These compounds can be regarded as phosphorus analogues of aromatic imides, which are recognized as prominent electron-transporting organic dyes.[2] Herein we present the synthesis of this new class of organophosphorus compounds and their physicochemical properties.[3]

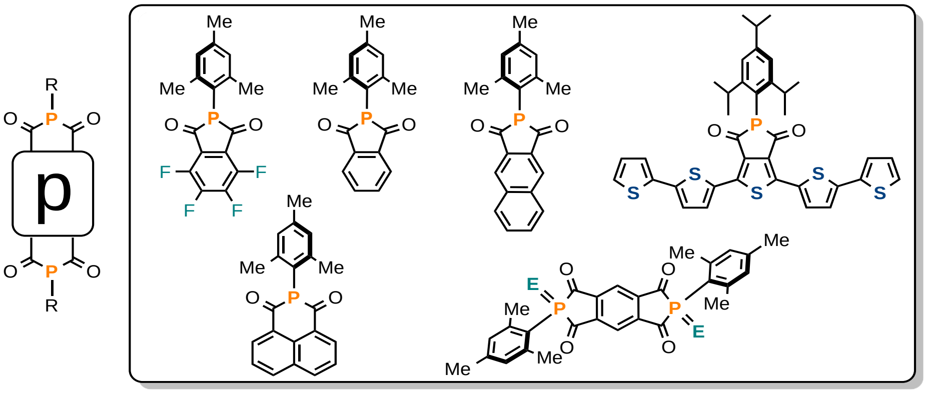

Fig. 1. Developed Diketophosphanyl Compounds

Acknowledgements

This research is supported by a Grant-in-Aid for Scientific Research on Innovative Area "π-Systems Figuration: Control of Electron and Structural Dynamism for Innovative Functions" (KAKENHI Grant Number JP15H00997) from the Ministry of Education, Culture, Science and Technology (MEXT), Japan. The author also acknowledge the financial support from the Shorai Foundation for Science and Technology.

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STIMULATED EMISSION OF DCM DERIVATIVES IN PVK MATRIX

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One of the well-known red light emitting laser dyes is 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) [1,2]. Amplified spontaneous emission (ASE) had been widely investigated of DCM molecules or its derivatives in polymer or low molecular weight matrix. The main issue for these molecules is aggregation which limits doping concentration in matrix. Lowest ASE threshold values within concentration range of 2 and 4 wt% were obtained [3].

In this presentation we will show ASE properties of three original DCM derivatives in poly(N-vinylcarbazole) (PVK) at various concentration. Two of the derivatives are the same DCM dye with replaced butyl groups at electron donor part with bulky trytiloxyethyl groups and with (DWK-1) and without (DWK-1TB) replaced butyl group at pyran part by terc-butyl group. These groups do not influence electron transitions in the dye but prevent aggregation of the molecules. Third derivative (DWK-2) consists of two equal donor groups with the attached trytiloxyethyl groups. All results will be compared to DCM:PVK systems.

Photoluminescence quantum yield (PLQY) is almost three times larger for DWK-1 and DWK-1TB concentration up to 20wt% with respect to DCM systems. PLQY was saturated on 0.1 at higher DWK-1 and DWK-1TB concentrations. Bulky trytiloxyethyl groups prevent aggregation of the molecules thus decreasing interaction between dyes and numbers of nonradiative decays.

Ekspla 310 series laser at 532 nm with repetition rate 10Hz and pulse duration 10 ns was used as light source for ASE measurements. The irradiation area on surface of the sample was stripe form with dimension 4x0.4 mm2. Light emission was measured at the edge of the sample.

Increases of dye density in matrix with small lose in PLQY results in low ASE threshold energy. The lowest threshold value was obtained around 7 $\mu J/cm^2$ in DWK-1TB/PVK films.

Influence of the molecule structure on PLQY and ASE threshold value in the doped thin films with various concentrations will be discussed.

Acknowledgements

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AgInZnS QUANTUM DOTS AS COMPOUNDS IN BULK HETEROJUNCTION PHOTOVOLTAICS

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Hybrid organic/inorganic solar cells utilizing quantum dots (QDs) have been extensively studied recently with an aim to extend sensitivity to longer wavelengths. However majority of QDs reported in literature contain chemical elements such as Cd, Pb or Hg which are hazardous to human health and the environment. Therefore, fabrication of electronic devices using only non-toxic compounds constitutes an important challenge [1]. The main aim of our research is to obtain solution-processible active materials for solar cells and photodiodes based on greener nanoparticles (Cd- and Pb- free), combined with conjugated polymers whose chemical structure allows for an efficient photovoltaic cell operation and long-term stability of the devices in ambient conditions.

In the presented work we describe the performance of hybrid solar cells with AgInZnS QDs. The AgInZnS nanoparticles were synthesized by a typical hot-injection approach, i.e. a solution of elemental sulfur in oleylamine was rapidly injected to a preheated solution of silver(I) nitrate, indium(III) chloride, zinc stearate and 1-dodecanethiol in 1-octadecene. As obtained nanocrystals were isolated by precipitation and subjected to a ligand exchange process, in which primary ligands were substituted by pyridine or n-butylamine [2]. QDs with pyridine ligands (which also play the role of solvent for the nanoparticle suspension) have sizes in the range from 1.5 to 4 nm. In our studies QDs were mixed with poly(3-hexylthiophene-2,5-diyl) (P3HT). The active layer was spin-coated on a patterned indium tin oxide (ITO) substrates onto which PEDOT:PSS had been previously deposited. In the last step a 20 nm layer of calcium or 100 nm layer of aluminium (which served as a cathode) was deposited by evaporation. The devices were measured with a sunlight AM 1.5 simulator and all the described steps were undertaken under a controlled nitrogen atmosphere in the glovebox system.

Acknowledgements

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ELECTROACTIVE POLYMER BASED MAGNETIC TRIPLE COMPOSITES

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Nanocomposites based on nanoparticles made from magnetic metals are promising for various potential applications such as spin-polarized devices, carriers for drug delivery, magnetic recording media, high-frequency applications, magneto-optical storage, interference suppression, biomedical sensing, etc. Magnetite, Fe_3O_4, is a promising material for anodes and spintronics due to its high theoretical capacity, high density, low cost, low toxicity, and good magnetic properties.

We prepared composite films made from polymer, graphene nanoplatelets (GNP) and magnetite nanoparticles and formed in magnetic field. Fe_3O_4 nanoparticles have average diameter of about 7 nm and represent a magnetic liquid in hexane. This liquid is very sensitive to magnetic field resulting to high ordering of iron oxide nanoparticles. GNP-Fe_3O_4 composite has been obtained by mixing of GNP and magnetic liquid with 1:1 ratio followed by sonication and mixing with polymer solution. Then composite solution was dropped on Si or quartz substrate. Thin films are formed by drying in air in magnetic field or without it. It was found that thin film formed in magnetic field has more porous structure and active surface as compared to film without this field.

It was shown that magnetic field applied to samples during film formation effects strongly electric properties of these films. Thin films formed without magnetic field has activation character of conductivity, while thin films formed in magnetic field has metallic type of conductivity. Thus, magnetic field acting during film formation in these composites results in metal-dielectric transition.

Magnetic properties of these composites are also presented and discussed.

3,3’-BICARBAZOLE DERIVATIVE AND ITS MIXTURES WITH DONOR AND ACCEPTOR MOLECULES FOR TADF OLEDs

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Organic light-emitting diodes (OLEDs) are utilized in display and lighting technologies despite their lower efficiency and life-time compared to those of LEDs [1]. Recently, thermally activated delayed fluorescence (TADF), which can be obtained in a single molecule and in the mixtures including donor and acceptor molecules, have been discovered to overcome the bottleneck of OLEDs [1]. The further progress in this field requires development of efficient emitters and the search for new approaches for TADF OLEDs. Carbazole derivatives could be promising candidates as TADF emitters for OLEDs due to their optical, electrochemical, thermal, charge-transporting properties, energy levels etc. For example, carbazole-based compound tri(9-hexylcarbazol-3-yl)amine (THCA) has recently been used for the preparation of TADF emitting layer for a novel double-layer exciplex-based OLED [2]. In addition, THCA has been applied as a component of TADF emitting layers for the formation of a “warm-white” OLED [3].

This work is on 3,3’-bicarbazole derivative which showed efficient emission with greenish blue color. We found that the TADF effect was observed in the emission of this derivative due to a small value of ΔE_{ST} (~0.06 eV). In addition, because of the ambipolar properties of the 3,3’-bicarbazole derivative, exciplexes having TADF were identified in a mixtures between the carbazole derivative and the donor 4,4′,4″-tris[3-methylphenyl(phenyl)amino] triphenylamine (m-MTDATA) or acceptor 2,9-dimethyl-4,7 diphenyl-1,10-phenanthroline (BCP). This finding allowed us to develop a new approach for the fabrication of effective TADF OLEDs. We fabricated OLEDs which showed a low turn-on voltage of 2.8 V for electroluminescence at 1 cd/m^2, maximum external quantum efficiency values of 6.29 % and a maximum brightness of 34 500 cd/m^2 at 15 V utillizing the synthesized 3,3’-bicarbazole derivative and its eciplexes.

Acknowledgment
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DESIGN OF GLASS-FORMING HIGH-TRIPLET-ENERGY DERIVATIVES FOR OPTOELECTRONICS: EXPERIMENTAL AND THEORETICAL APPROACH

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Effective harvesting of both singlet and triplet excitons still is one of the main goals in organic light-emitting diodes. Efficiency of the devices can be dramatically improved employing triplet excitons through intersystem crossing [1] or reverse intersystem crossing (thermally activated delayed fluorescence) [2] mechanism in high-triplet-energy materials.

In this work, a series of new high triplet energy D-A-D derivatives were synthesized by incorporating different electron acceptor units (dibenzofuran and thioxanthene derivatives) and donor moieties (methoxycarbazole, phenothiazine, phenoxazine or acridine), Fig 1. All compounds were investigated using density functional theory and the comparative experimental study was performed.

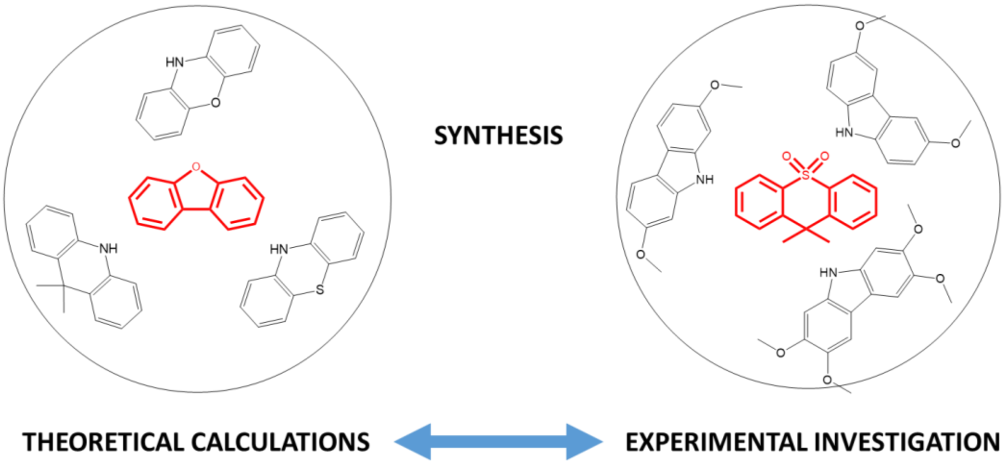

Fig. 1. Different electron acceptors and donors

Due to very small theoretical/experimental singlet-triplet energy splitting (~0.1-0.2 eV) new D-A-D molecules were analyzed as potential candidates for organic light-emitting diodes based on thermally activated delayed fluorescence.

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APPLICATION ORIENTED FUNCTIONAL MATERIALS FOR FEMTOSECOND LASER 3D MICRO- AND NANOFABRICATION

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The rapid advancement in ultrafast laser material processing brought the world the capability to fabricate true 3D polymeric micro- and nanostructures. Technology applied for this, 3D laser lithography (3DLL), have proven to be capable of delivering objects suitable for usage in broad range of applications, including biomedicine, microoptics and photonics [1]. In most cases standard 3DLL polymers are employed for the manufacturing which include hybrid organic-inorganic photopolymers [2] or common in UV lithography SU-8 [3]. In such cases the design and/or architecture of the structure is tailored in order to maximize its effectiveness and minimize the deficiencies of the material used. For example, flexible 3D object can be fabricated from the hard material adopting chainmail-like design [1] or suspended high aspect ratio cantilevers.

We present an approach of altering the material to best suit the final application. One of the examples is doping polymers with noble metal nanoparticles (NP) [Fig. 1 (a)]. Because of their strong plasmonic interaction with light gold NP generate relatively strong optical response even when their concentration is as low as $\sim 10^{-3}$ wt% [4]. Also, in comparison to organic dopants (for example fluorescent dyes) NP do not degenerate over time and grant consistent optical properties independent from the duration of the experiment. Another example is special highly resilient polymer designed for 3DLL. Hard gel form during fabrication, possibility to structure it without addition of photoinitiator and low shrinkage during development [3, 4] provides such material with superb mechanical strength [3] and high optical damage threshold [5]. This is crucial for rapid development of scientific/technological fields of microoptics on non-standard substrates (for example facets of the optical fiber) [Fig. 1 (b)] or optomechanics [Fig. 1 (c)].

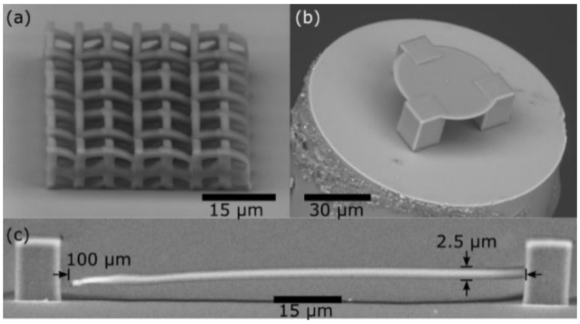

Fig. 1. (a) Intricate 3D structure produced with femtosecond laser out of SZ2080 doped with $3.9 \cdot 10^{-3}$ wt% gold NP. Fabrication from the nanocompound combining polymer and gold NP shows no influence on the mechanical quality of the microstructure [4]. (b) – 3D microoptical element on the facet of the optical fiber. (c) – side view of high aspect ratio (~100 μm long and ~2.5 μm thick) cantilever for optomechanical applications. (b) and (c) structures are fabricated out of non-photosensitized SZ2080.

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MOLECULARLY IMPRINTED POLYMERS FOR BIOSENSING

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The technique of molecular imprinting has been being developed at the Department of Materials Science, Tallinn University of Technology. This new technique allows for the preparation of polymeric materials with specific binding sites for a target molecule, Molecularly Imprinted Polymers (MIPs). The research group integrates MIP-based synthetic receptors with sensing platforms like QCM, SPR, SAW to selectively recognize biomacromolecules (proteins, antibodies) as well as small molecules (pharmaceuticals, amino acids, nucleic acids). The development of MIP-based biosensor has evident potential applications in biotechnology and medical diagnostics (e.g. hepatitis, cancer) due to robust design, inexpensive and easy preparation, multiplexing capability, possibility to offer detection of analytes for which no receptor is available.

The integration of MIP with a sensor transducers, for example piezoelectric or optical, leads to a highly selective chemical sensors that can be assembled into water treatment reactor or air pollutants for online monitoring of the trace concentrations of selected pollutants.The activities of the MIP group will be addressed to the elaboration of highly selective MIP materials through application of different imprinting strategies allowing their integration with various sensor transducers in order to develop an on-line monitoring system with unprecedented performance at good reversibility and suitable response times.

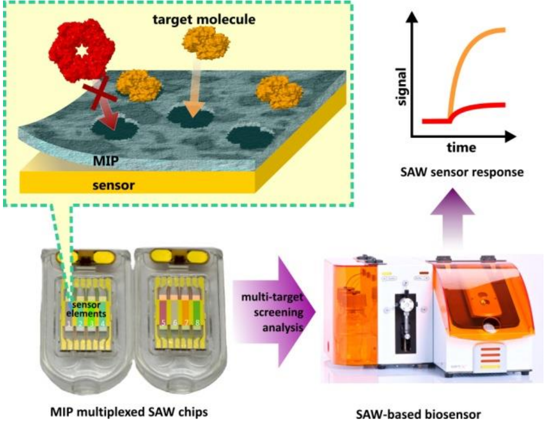

Fig. 1. Modification of the sensing elements with responsive MIP coatings selective towards different targets allow multi-target screening analysis up to 8 different substances with extremely high sensitivity.

The synergistic effect of combining molecular imprinting and surface acoustic wave (SAW) technologies for the selective and label-free detection of antibiotics in aqueous environment was demonstrated for the first time.

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LOW BAND GAP (X-DADAD)$_N$ TYPE COPOLYMERS FOR STABLE AND EFFICIENT BULK HETEROJUNCTION ORGANIC SOLAR CELLS

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Organic solar cells based on conjugated polymers demonstrated efficiencies approaching 8-10%. Unfortunately, the best-performing materials undergo rapid photochemical degradation. On the contrary, long operation lifetimes (7-15 years) have been projected for some less efficient polymers possessing robust chemical structures, e.g. PCDTBT.

In the present talk we will present our strategy of designing PCDTBT-like polymers with narrowed band gaps using alternating DADAD architectures as building blocks (D – electron donor such as thiophene, while A is an acceptor like benzothiadiazole or benzoxadiazole) [1-3]. Synthesized polymers demonstrated diverse optoelectronic and photovoltaic characteristics. The best materials showed solar cell efficiencies approaching 7% in combination with long-term operation stability. Higher performances of 10-11% are feasible for single junction devices due optimal band gaps (1.60-1.65 eV) and deep-lying HOMO energy levels (~ -5.5 eV) of the designed materials.

The developed polymers enabled fabrication of larger area solar cells under ambient conditions in air using slot die coating which is a roll-to-roll compatible film deposition technology [4]. The roll-coated devices exhibited impressive power conversion efficiency of >6%.

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CHALCOGENOPHENE-BASED D-A-D MONOMERS WITH PYRIDINE ACCEPTOR UNIT

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Thiophenes are known from their interesting electrochemical properties as well as from numbers of possible applications in areas such as OLEDs or OPVs. The thiophene-based monomers, that possess thiophene rings with unprotected 5- position can easily polymerize with formation of stable films. The properties of the films such as electrochromism, charge mobility, band gap, can be tuned by addition of different electron-donating or electron-accepting groups, alkyl chains and others. However, in another approach the sulfur atoms of thiophenes are substituted by heavier chalcogens, such as selenium or tellurium.

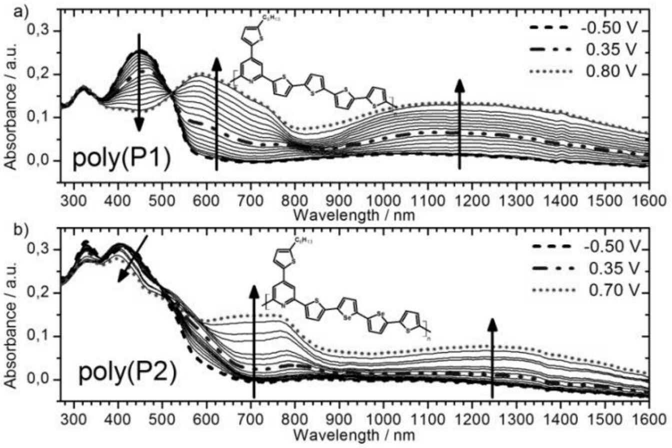

Fig. 1. Electrochromic response of the polymers under oxidation.

In this study we present spectroscopic and electrochemical properties of chalcogen-based monomers. One of the monomers has two sulfur atoms substituted by selenium. The differences between the monomers caused by the type of chalcogen atom used are described and explained. Steady state and time-resolved spectroscopic as well as electro- and spectroelectrochemical methods are used to study the properties of described systems.

Acknowledgements

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EXCILIGHT

3D SCAFFOLDS IN RECONSTRUCTION OF THE LARYNX

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Implantation artificial larynx is one way to avoid problems after resection due to: cancer benign tumors, injures. Mentioned problems are: nonphysiological way of breath (tracheotomy tube is necessary) voice communications deficit, swallowing problems. Nowadays there are many devices which can replace function of the larynx. They can made from variety materials and dived into outside – electrolarynx and inside – implants of the larynx. Efficient implant have to be completely biocompatibility and personalized for each patient. Artificial porous scaffold larynx covered with collagen and chondrocytes is a new solution in this way of treatment figure 1. This work is focused on novel polymer blend material that could be used as filament in 3D printers and extrusion feedstock. For now there are only some materials, like a polylactide (PLA), copolymer acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS), nylon or commercial plastics like laywood and laybrick, that are generally used in 3D printers. Instead of it we propose medical, biocompatible PC as a matrix for novel material, however disadvantages of this polymer would make it difficult to use in pure form.

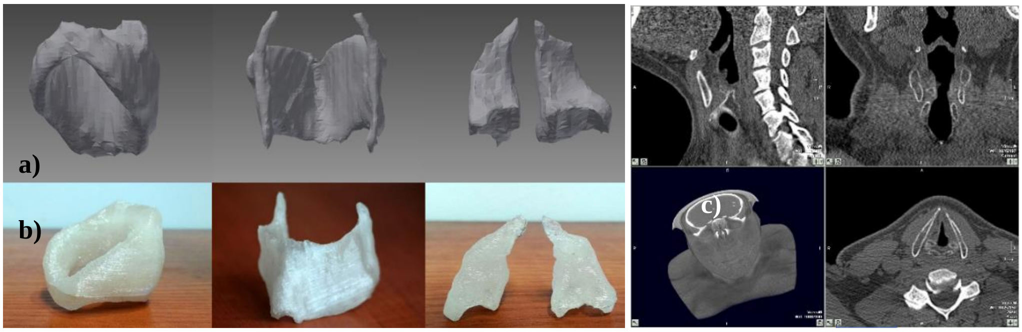

Fig. 1. Reconstruction of cartilage of larynx: a) microtomography model b) real model after 3D reconstruction c) tomography (CT) of neck in 3 layouts and volume scan.

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NON-LINEAR SUGAR-CENTERED POLYMETHACRYLATES AS CARRIERS FOR ANTICANCER DRUGS - THE ROLE OF THE STRUCTURE IN PHYSICOCHEMICAL PROPERTIES AND DRUG RELEASE

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Controlled polymerization techniques have gained opinion to be convenient in designing polymers with sophisticated structures towards their potential use as drug carriers. Atom transfer radical polymerization (ATRP) and insertion-coordination ring opening polymerization (ROP) have been used in order to obtain V-shaped and star-shaped homo- and miktoarm copolymers.[1] Next, post-polymerization modifications allowed the introduction of specific functional groups (carboxyl or amine) that induced amphiphilicity and provided possibility of chemical conjugation or encapsulation of chosen drugs, i.e. doxorubicin (DOX), methotrexate (MTX), camptothecin (CPT).[2,3] The physicochemical properties of obtained conjugates and aggregates were examined in order to find correlation between size, charge, shape (aggregates) or binding constant (conjugates) and the structure of polymeric matrix. Furthermore, the drug release kinetic profiles allowed evaluate the influence of the arm composition and abovementioned properties on the rate of drug release.

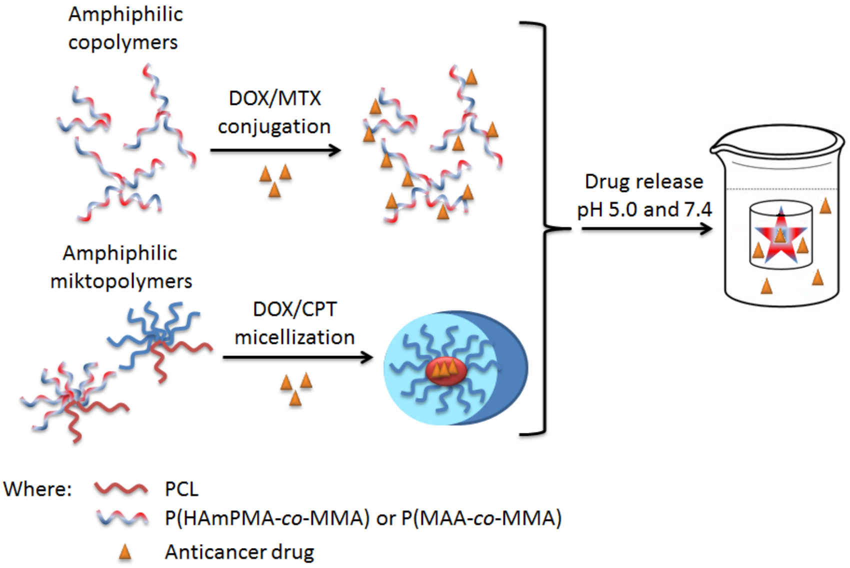

Fig. 1. The anticancer drug incorporation and release from obtained homo- and miktoarm star-shaped copolymers

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POLY(2-HYDROXYPROPYLENE IMINE) DERIVATIVES CONTAINING SEGMENTS OF PEG AND/OR CYSTAMINE AS EFFICIENT REAGENTS FOR DNA/siRNA TRANSFECTION

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Polymeric carriers for delivery of DNA / siRNA to cells belong to hot topics in polymer science. The ideal polymeric carrier must contain proper molecular weight, structure and protonation ability for achieving long circulation time, low immunogenicity, good biocompatibility, selective targeting and efficient penetration of physiological barrier [1].

Poly(2-hydroxyalkylene imines) possessing both imine and hydroxyl groups in their repeating units have been synthesized recently and shown to be efficient gene transfection reagents [2]. More detailed examination of poly(2-hydroxypropylene imine) (PHPI) revealed that at higher concentrations it showed substantial cytotoxicity [2]. Trying to overcome this problem, modification of PHPI by the segments of metoxy poly(ethylene glycol) (MPEG) and/or cystamine (CA) was foresee, which could make the polymers more hydrophilic, non-immunogenic and biodegradable.

PHPI containing segments of MPEG (M_n 1000, 2000, 5000) and/or CA were synthesised using 1,3-diamino-2-propanol (DAP), 1,3-dibromo-2-propanol, MPEG iodide and cystamine as starting materials. Addition of MPEG iodide to the initial mixture of the monomers or during the final stage of polycondensation enabled to synthesize PHPI derivatives with different MPEG content and various molecular weight [3]. Variation of the ratio CA to DAP enabled to synthesize PHPI-CA with different amount of disulfide bonds. PHPI derivatives were characterized by FTIR and NMR spectroscopy, SEC, DLS, DSC and potentiometric titration, and were tested for DNA and siRNA delivery *in vitro*.

It was shown that PHPI-MPEG and PHPI-CA were highly branched polymers containing MPEG segments and/or disulfide linkages. Attachment of MPEG had a positive effect on siRNA delivery: high-molecular-weight polymers with low content of MPEG performed significantly better than PHPI and low-molecular-weight polymers with high content of MPEG [3]. Transfection efficiency of PHPI-CA for DNA gave similar results to that of PHPI reaching 80-90% but cytotoxicity levels for PHPI-CA were substantially lower. PHPI-CA containing different amount of disulfide linkages were able to break down and release DNA following the treatment with reducing agent DTT suggesting that these polymers could be great candidates for *in vitro* and *in vivo* transfection.

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MODELING FATIGUE OF CARBON FIBER COMPOSITES UNDER TENSILE LOADS

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Carbon fiber composites are utilized in various applications and in some cases, such as composite overwrapped pressure vessels (COPVs), the sustained and cyclic loading are predominantly tensile. The COPVs may be exposed to low-velocity impact damage reducing their short and long-term residual strength. Currently, no modeling approach for assessing the long-term performance of damaged COPVs under cyclic loads has become universally accepted by the community. In this work, a finite element (FE) based analysis is proposed for modeling the reduced fatigue life prognosis after impact. The fatigue modeling aspect is focused on, damage is simply represented by notches or holes.

The ply-level failure of composites in tension consists of fiber failure, delamination and matrix cracking as the main failure mechanisms. The implemented fatigue analysis considers two mechanisms: fiber tensile failure (FTF) and delamination (DL) between layers of different fiber orientation. A state of saturated matrix cracking is assumed to be initially present in the composite, a realistic assumption for highly loaded structures, such as COPVs after the factory testing.

The FE analysis and the general program logic is implemented by using Abaqus software and its Python-based Scripting Interface. When modeling fatigue, the stiffness degradation occurs in discrete steps for individual elements, as the remaining life becomes zero. The remaining fatigue life is calculated by a Miner sum and by relevant SN-curves for FTF and DL mechanisms. The damage growth and the final failure are simulated under force controlled tensile fatigue for a simple tensile specimen, a notched and a central-hole specimen. The current study looks into the behavior of tensile laminate specimens, preceding later investigations with a specific focus on the COPVs.

Acknowledgements

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SYNTHESIS AND APPLICATION OF PLASTIFIERS FOR CONCRETE MIXTURES ON THE BASE OF ACRYLIC COPOLYMERS

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The problem of improving the flow characteristics of concrete mixtures is directly connected to aggregate stability of concrete suspensions. Earlier it was achieved by using lignosulfonates and the sodium naphthalenesulfonate-formaldehyde condensates. However the polymers containing long hydrophilic substituents are more effective as such admixtures and allow the reduction of the water to cement ratio and the increasing the strength of concrete. In addition to hydrophilic substituents such polymers must have "anchor" groups to bind to concrete particles surface. In this study copolymers of acrylic acid (AA) and methoxy poly(ethylene glycol) methacrylate (MPEGMA) were investigated as the objects answering both the conditions. The main problem which occurs on the way of their application is a strong requirement to the copolymers molecular mass (MM). MM must be low enough to stabilize the suspensions as it is described at Fig.1, otherwise polymer will provoke flocculation (Fig.1, right).

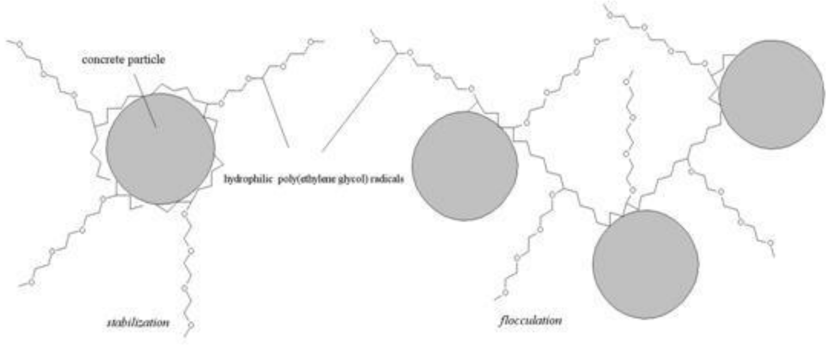

Fig. 1. The mechanism of action of low and high-molecular AA-MPEGMA copolymers in concrete suspensions

The second problem is a low composition homogeneity of poly(AA-MPEGMA) because of the difference in the monomers reactivity ratios. Here we propose to solve the first question obtaining the copolymers in water solutions in the presence of copper (II) ions which cause termination of material chains by disproportionation of growing radicals and decrease polymer molecular mass. Termination mechanism and polymerization kinetics were studied in detail. Copper (II) ions work as "an ideal terminator", practically not influencing on kinetics. The second question was be solved by using the compensation way of polymerization (gradual dosing of more active monomer (AA) during the reaction).

For the fist time RAFT polymerization was used to resolve both the problems together. The copolymers MM was effectively controlled by concentration of RAFT agent: the higher concentration was the lower molecular mass. Composition homogeneity of copolymers was a result of RAFT polymerization mechanism.

THE INFLUENCE OF THE LINKER ON PROPERTIES OF D-A-D TYPE *S*-TETRAZINE DERIVATIVES

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S-tetrazine is a well-known compound in many fields of applications such as explosive materials, coordination chemistry, organic chemistry (retro Diels-Alder cyclisation), optoelectronics.[1] *S*-tetrazine also displays a strong electron-withdrawing character. It undergoes reversible electrochemical reduction at high to very high potential which is associated with low-lying LUMO level.[2,3] Moreover, *s*-tetrazine derivatives are often colored and sometimes fluorescent.[4,5] Functionalization *s*-tetrazine ring with electron donating groups leads to obtain ambipolar compounds which are very useful in terms of (opto)electronics applications. Keeping it in mind, we designed and synthesized D-A-D type of triphenylamine-*s*-tetrazine derivatives.

We report on electrochemical (cyclic voltammetry-CV, differential pulse voltammetry-DPV) and spectroelectrochemical (UV-Vis, EPR, Fluorescence, Raman) investigations of bipolar triphenylamine-*s*-tetrazine derivatives with various linkers between donor and acceptor units. Our investigations allowed to specify the impact of the nature of the linker between donor and acceptor units on properties of investigated molecules. The electrochemical analysis indicated that such type of s-tetrazine derivatives undergo electrochemical polymerization (oligomerization). However, a significant effect of a chemical structure on the electrochemical polymerization process as well as on electrochemical properties of electropolymerized films was observed. Additionally, in order to conduct more precise analysis of experimental results the DFT/TDDFT calculations were carried out.

Acknowledgements

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EXCILIGHT

THERMOLUMINESCENCE SPECTROSCOPY STUDY OF CONJUGATED POLYMER FILMS: WHAT CAN WE LEARN FROM THESE MEASUREMENTS?

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This report provides an overview of thermally-stimulated luminescence (TSL) studies we have performed in conjugated polymer films and discusses in details physical process responsible for the TSL phenomenon in these materials. We show that TSL can be an important method for characterization of charge-carrier traps and energetic disorder in conjugated polymer films. Charge trapping was investigated by the TSL technique in a broad range of organic semiconducting π- and σ- conjugated polymers including technologically important optoelectronic polymers as substituted poly(paraphenylene), different substituted poly(phenylene-vinylenes), poly(thiophenes), poly(fluorenes), poly(silylenes), as well as in conjugated polymers doped with phosphorescent emitting metal-organic complexes. The obtained results are interpreted in terms of the thermally assisted hopping model of TSL we have developed before and we show that analysis of the TSL data allows evaluating of very important material parameters regarding the Density-of-State (DOS) distribution profile and charge-carrier trap energies in these semiconducting materials. The results of TSL studies are found to coincide well with that determined from conventional charge transport studies.

Topics covered in this report: (i) origin of energetic and positional disorder in conjugated polymers; (ii) Anderson localization, hopping transport concepts and Miller-Abrahams jump rate; (iii) basics of Gaussian disorder formalism with application to conjugated polymers; (iv) TSL experimental method and its application for charge trapping study and evaluation of the DOS distribution in conjugated polymers; (v) our theoretical model of TSL and thermally-stimulated current (TSC); and (vi) critical comparison of different TSL models proposed in literature and fallacies underlying them.

Finally, I will demonstrate the application of TSL for evaluation of the energy splitting separating the singlet and triplet states of the interchain polaron pairs, which are the precursors of the electroluminescent species in conjugated polymers.

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NEW ORGANOSILICON POLYMERS AND COMPOSITE MATERIALS ON THEIR BASIS

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Hybrid organic-inorganic materials, where molecular organic and inorganic fragments are combined, have been considered potentially attractive for the purpose of developing new materials with a broad spectrum of interesting properties. In comparison with organic and inorganic constituents and polymers separately, hybrid organic-inorganic materials have a lot of advantages.

Polysiloxanes are of particular interest due to their extremely low glass transition temperatures and flexibility, their hydrophobic surface properties, good thermal stability and excellent flame retardant. The properties of organosilicon polymers depend on the structure of a macromolecular chain and of the nature of the surrounding organic groups at silicon atom.

Widely applied hydrosilylation reactions of polymeric systems with dienes have attracted great interest due to the practical outcome. From above mentioned it is evident that synthesis and investigation of new polysiloxanes with double bond containing fragments attracts much attention due to their wide applications in cross linking processes initiated by peroxides. From this point of view the chemical modification reactions of poly(methylhydro)siloxanes (PMHS) as well as poly-dimethyl(methylvinyl)siloxanes is very interesting.

In presented paper, we have investigated the modification of PMHS via hydrosilylation reactions with conjugated and un-conjugated dienes in the presence of platinum catalysts, new organosilicon methylsiloxane oligomers with reaction able un-saturated side groups have been obtained. As well as modification reactions of polydimethyl(methylvinyl)siloxanes have been carried out. On the basis of obtained methylsiloxane polymers with un-saturated side group's filled electro conducting composite materials have been obtained and studied.

Acknowledgements

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SOME APPROACHES AND RESULTS ON DESIGN OF EMITTING POLYMER COMPOSITES FOR OLEDs

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Main requirements for the emitting layers for OLED are high efficiency, good color characteristics, sufficient lifetimes, suitable mechanical properties like for example flexibility and sufficiently low cost. Some of these requirements are still not quiet reached for the technology: relatively low lifetimes of blue emitters, relatively low efficiency of single-layer emission while at the same time energy losses at the interfaces of multilayered emission layers, relatively high price of the most commonly used compounds etc.

One of the promising types of OLED architecture is polymer(host)/dyes(guest) approach. It allows to create single-layer polymer-based emitting layer for OLED with less interface energy losses comparing to multi-layered devices, better control of excitation energy transfer, better mechanical properties etc. In such approach the most important process to be controlled and developed is excitation energy transfer (EET) from polymer matrices to light emitting centers. EET strongly influence on all main properties of the emitting layer: efficiency, color characteristics and lifetime. One of the goals in developing efficient emission layer due to this approach is to make the optimal concentration of guest molecules – such as all the excitation energy goes directly to the luminescent dye molecules. There are two main analytical approaches which could help to estimate optimal concentration of guest dye: Powell model which was adapted to real conditions in the polymer media by Yashchuk V.M. and Slobodyanik V.V. in 1984 and model of one-dimensional diffusion of Frenkel excitons in macromolecules first proposed and experimentally confirmed by the same authors in 1982. Both of them could be used to estimate optimal dye concentration due the luminescence data of polymer matrix and guest-dyes.

Other way to increase efficiency of single-emitting layer of OLED is to improve luminescence quantum yield of the guest molecules. For this goal Boron-containing compounds could be used due to their specific properties of making a hard frame and increase the luminescence quantum yield of the host molecules. Also compound with close energy position (<0.1eV) of first excited triplet and singlet levels could be used to increase internal quantum efficiency due to thermally activated delayed fluorescence (TADF).

One more perspective way of using single emitting layer architecture in OLEDs is to create White OLEDs. The main problem of this approach is lack of dyes which emission could cover all visible spectral range alone and difficulties in managing correct EET between different dyes if few different guest dyes are used. Two main approaches are being used to solve these problems: developing a molecule with few different luminophore groups or using molecules with proton/electron transfer. First way allows obtaining sum of the each chromophore luminescence and thus obtaining “white” light curve. Another approach is to use ESIPT-dyes (Excited State Intramolecular Proton Transfer) like diflavonols or aminoxanthones. Due to its specific properties such dyes luminescence could cover nearly all visible spectral range and so they could be used in single layer WOLEDs as the only guest emitter.

HYBRID SOLAR CELLS BASED ON a-Si AND ELECTRODEPOSITED POLYPYRROLE

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Hybrid solar cells combine the advantages of organic and inorganic materials in order to obtain efficient solar cells at low cost. A hybrid solar cells (polypyrrole (PPy)/i-Si/n-Si/AZO/glass) with a *p-i-n* junction structure have been prepared and investigated. Amorphous Si was used as substrate with n- and *i*- layers, which acted as a charge separation and photo-absorber layer, respectively. Doped PPy was deposited onto the i-Si layer using photo-assisted electrochemical deposition under a semiconductor red laser illumination (670 nm, 20 mW/cm^2, spot size 5 mm). Electrodeposition was held at room temperature in acetonitrile and aqueous solutions at the potential values of 300, 500 and 700 mV vs. SCE. At these potential values, PPy covers only illuminated area of a-Si. The best I-V parameters were obtained for the hybrid Si structures with PPy layer electrodeposited at 300 mV vs. SCE during 330 seconds in aqueous solution and doped with naphthalene-1-sulfonic acid sodium salt (NaNSA). The thickness of the electrodeposited PPy layer on amorphous i-Si is about 400-500 nm (Fig. 1). It should be noted that these structures including graphite as well as golden back contact have reproducible I-V parameters with photoconversion efficiency varying from 2.4% to 4.1%. The V_{OC} for the best graphite/PPy:NaNSA/i-Si/n-Si/AZO/glass structure is 722 mV, and power conversion efficiency of about 4.1%. The I-V parameters were measured under white light irradiation of 100 mW/cm^2 intensity.

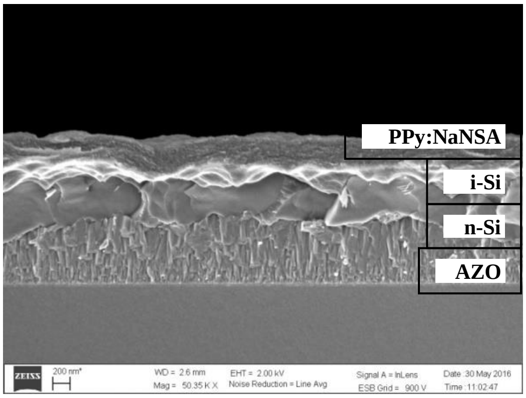

Fig. 1. Cross-sectional HR-SEM image of PPy:NaNSA/i-Si/n-Si/AZO/glass hybrid structure.

Acknowledgements

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MECHANICAL AND ELECTRICAL CHARACTERISTICS OF POLYETHYLENE/CARBON NANOTUBE NANOCOMPOSITE

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Polyethylene (PE)/carbon nanotube (CNT) nanocomposites have received considerable attention in research due to their anticipated mechanical [1] and electrical [2, 3] properties offering broad application range.

PE/CNT nanocomposites were prepared by melt-blending commercial PE Egyeuroptene MD 3804 U with CNTs Baytubes C 150 P by using two roll mill. Specimens for testing of physical properties were obtained by injection moulding and compression moulding.

Stress-strain characteristics were determined by Zwick/Roell BDO-FM 020TN machine, according to EN ISO 527. Dynamic mechanical thermal analysis (DMTA) was carried out by using Mettler Toledo DMA/SDTA861 to measure storage modulus E', loss modulus E'' and loss factor tanδ. Dielectric spectroscopy measurements were carried out isothermally in the frequency range 10^{-2}–10^{7} Hz by means of a Novocontrol Concept 50 impedance analyzer.

Stress-strain results of PE/CNT nanocomposites showed increase in modulus of elasticity E, ultimate tensile strength σ_B and yield strength σ_Y by increasing CNT content. Increment of these stress-strain characteristics were, however, hindered due to certain agglomeration of CNTs, especially at higher nanofiller contents.

Additional DMTA measurements showed increase in E' by increasing CNT content, most noticeable at low temperatures. E'' and tanδ revealed glass transition in temperature range -100 – -120^{o}C and secondary transition in the crystalline phase of the polymer matrix at 50^{o}C.

Dielectric spectroscopy showed nonlinear changes in dielectric permittivity ε' (Fig. 1.) by adding CNTs to PE matrix. AC conductivity σ' at 5wt.% CNT content became independent from frequency describing percolation threshold between 2 and 5wt.% of CNT content.

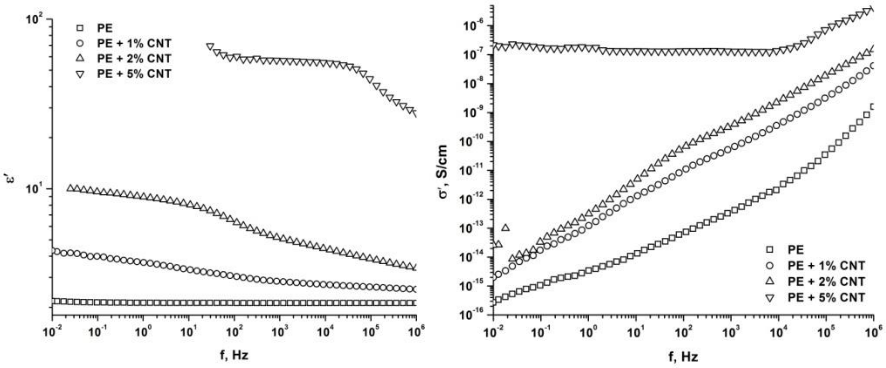

Fig. 1. Dielectric permittivity (ε') and conductivity (σ') as a function of frequency

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INTERGEL SYSTEMS IN SORPTION OF LANTHANUM IONS

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In intergel systems polymer hydrogels undergo mutual activation during remote interaction. Result of such activation is transfer of polymer macromolecules to highly ionized state. During mutual activation electrochemical and conformational properties of hydrogels are changed significantly. In an aqueous medium specific electric conductivity increases with time, and pH values firstly increases after that decreases. It occurs due to binding of cleaved protons from carboxyl groups by nitrogen heteroatoms of vinylpyridines. As a result functional groups with same charge repel with further unfolding of polymer chains. Consequently swelling coefficient of macromolecule also increases.

Study of intergel systems' selectivity in relation to lanthanum ions showed that electrochemical and conformational properties of hydrogels change in different way in comparison with hydrogels behavior in an aqueous medium. Obtained data showed that with time there is a decrease in values of electric conductivity. Concentration of hydrogen ions increases with time. Also there is decrease in hydrogels swelling during lanthanum ions sorption due to the fact that charged groups amount is decreased in result of metal ions binding.

In intergel system polyacrylic acid hydrogel (gPAA) – poly-4-vinylpyridine hydrogel (gP4VP) maximum selectivity to lanthanum ions occurs at gPAA:gP4VP=2:4 molar ratio. Extraction degree of lanthanum ions at this ratio is 94.04%. Intergel system polymethacrylic acid hydrogel (gPMAA) – poly-4-vinylpyridine hydrogel (gP4VP) has maximum sorption degree of lanthanum ions at hydrogels ratio 1:5, it's value is 90.34%. Intergel system polyacrylic acid hydrogel (gPAA) – poly-2-methyl-5-vinylpyridine hydrogel (gP2M5VP) has maximum selectivity to lanthanum ions at hydrogels ratio 4:2, sorption degree is 91.09%. In intergel system polymethacrylic acid hydrogel (gPMAA) – poly-2-methyl-5-vinylpyridine hydrogel (gP2M5VP) maximum sorption degree occurs at ratio gPMAA:gP2M5VP=3:3, sorption degree's value is 89.65%.

Obtained data shows that all studied intergel systems have high selectivity values (over 90%) in relation to lanthanum ions. It should be noted that extraction degree of lanthanum in intergel systems is much higher comparison with individual hydrogels of polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine. Individual hydrogels sorption degree of lanthanum ions is 67.71%, 66.28%, 66.05%, 63.65% for polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine hydrogels respectively.

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UTILIZATION OF MECHANICAL SHEAR AND ADDITIVES FOR RUBBER DEVULCANIZATION

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Devulcanization has long been considered as desirable means to recycle end of life tires, but conventional thermochemical methods show only limited success, while enzymatic, supercritical CO_2, microwave and other techniques remain experimental. Currently, mechanochemical processing appears as an alternative [1]. In this study an open roll mill X(S)K-360 (Wuxi Double Elephant Rubber and Plastic Machinery Co. Ltd., China) was used, composed of two rolls (900 mm x 360 mm OD) with a power of 30 kW, linear velocity of 27 cm / s and a sliding ratio of 1.25. The roll surface was made of tool steel ($R_a < 10$ µm) and the average gap between rolls was ~100 µm. The devulcanization procedure consisted of premixing 1 kg of truck tread buffings with (or without) 4% wt. of devulcanizing agent and processing them in the mill for a desired number of cycles with the roll temperature below 50 °C. The amount of mechanical shear is enough to partially disrupt the cross-links of rubber and devulcanize it [2], as evident by cross-link density reduction per ASTM D6814 [Fig. 1, A]. During shear without added chemicals, cross-links might recombine and cause rubber particle aggregation into a sponge or a sheet [Fig. 1, B]. Aggregation accelerates if heat builds up, which is common due to rubber elasticity.

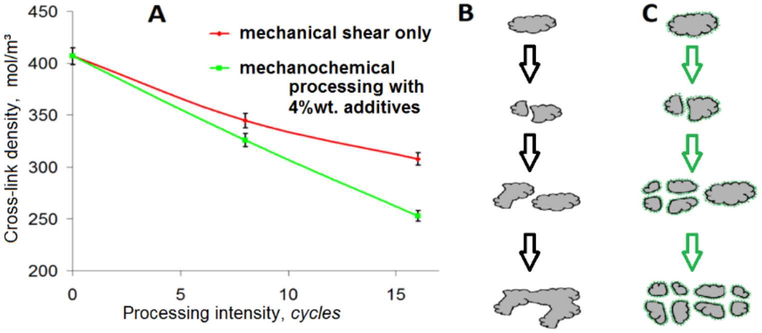

Fig. 1. Dependence between rubber's cross-link density and processing intensity (A); schemes of mechanical shear (B) without chemicals and mechanochemical processing (C) with electrostatically repelling additives.

Consequently, sheets of rubber are usually produced during mechanical shear. However, reclaim rubber powder is produced with the introduction of a devulcanizing agent [3], which suppresses particle aggregation, promotes cross-link delocalization and repels the particles electrostatically [Fig. 1, C]. Such powder has a much greater reuse potential than recycled rubber sheets and notably valorizes the concept of tire recycling.

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SYNTHESIS AND CHARACTERIZATION OF Au/CdS/D-g-PAA NANOHYBRIDS FOR BIOMEDICAL APPLICATIONS

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Semiconductor NPs (NPs) because of their unique electronic, optical, and catalytic properties are of great interests for both fundamental research and industrial development: utilization in the areas of light-emitting diodes, electroluminescent devices, lasers, hydrogen producing catalyst. Concerning the biological applications of NPs, there are biosensors and labels in biological imaging, probes for exploring DNA structures and immune diagnosis. However, for medical applications, use of inorganic nanoparticles still has many obstacles. Unfortunately, cadmium based NPs are toxic due to the release Cd^{2+} ions. In order to minimise their cytotoxicity and ecotoxicity inorganic nanoparticles are usually coated with protective coating. Natural polymers, synthetic polymers and gold are commonly used for coating NPs because these materials are non-toxic and relatively inert inside human body.

Here, we report the easy and economic synthesis of Au, CdS NPs as well as Au/CdS hybrid nanocomposites into branched D-g-PAA polymer matrices and present the results of their complex investigation. The size and shape of NPs are actually controlled by the choice of the synthesis route, the protection agent and the synthesis conditions. TEM and DLS of Au/CdS/D-g-PAA nanocomposites revealed complicated nanocomposite structure consisting of the Au nanoparticles (NPs) of 6 nm in size surrounded by small CdS NPs with size of 3 nm. These nanocomposites formed the aggregates-clusters with average size of 50–800 nm. Optical absorption spectra of Au/CdS nanocomposites consist of three absorption bands at 417 nm, 460 nm, and 548 nm bands originated from the excitons in CdS NPs and surface plasmons in Au ones respectively. The surface plasmon band of gold NPs are red shifted and broadened in Au/CdS/D-g-PAA nanocomposites comparing to one of Au NPs in Au/D-g-PAA proving the fact of close location of CdS and Au NPs in the synthesized Au/CdS/D-g-PAA nanocomposites. The Photoluminescense (PL) spectra of Au/CdS nanocomposites originate from the radiative transitions in excitons in CdS NPs. The 4-fold increase of intensity of free exciton PL is observed for CdS NPs in Au/CdS/D-g-PAA comparing to CdS ones in CdS/D-g-PAA that is due to PL enhancement by local field of surface plasmons in Au NPs. As well, the 12-fold decrease of intensity of localized exciton PL is observed for CdS NPs in Au/CdS/D-g-PAA comparing to CdS ones in CdS/D-g-PAA. Most probably, it is due to passivation of the surface of CdS NPs carried out by the Au ones.

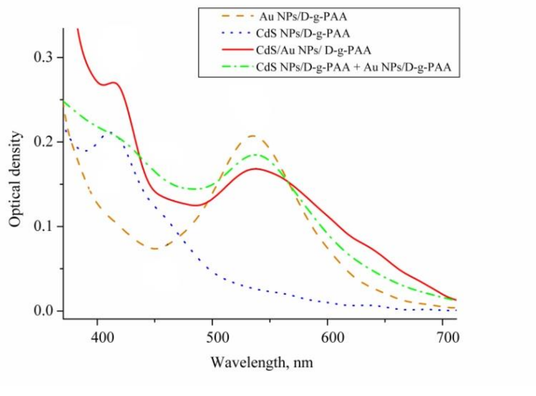

Fig. 1. Absorption spectra of CdS/Au NPs/D-g-PAA hybrids (solid line), Au NPs/D-g-PAA (dashed line), CdS NPs/D-g-PAA (dotted line) and mixture of CdS/D-g-PAA and Au/D-g-PAA NPs (dash-dotted line) dispersed in water.

CONJUGATES OF LIPOSOMES, POLYLYSINE AND MICELLES OF POLY-L-LACTIDE–POLYETHYLENEOXYDE BLOCK COPOLYMERS. FORMATION, BIODEGRADATION AND TRANSPORT PROPERTIES

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Liposomes are widely used in medicine and biology for encapsulation of bioactivee compounds. Liposome concentration within a rather small volume could help to increase the efficacy of liposome uptake by cells and therapeutic effect of a liposomal drug. In this work we describe biodegradable core–shell multiliposomal conjugates (MLC), that were obtained via electrostatic binding of a liposome‒polylysine complex with micelles formed of a poly-L-lactide–polyethyleneoxyde–poly-L-lactide triblock-or poly-L-lactide–polyethyleneoxyde diblock-copolymer. The citotoxicity and stability of conjugates of both types in a water‒salt media were analyzed. The rates of biodegradation of both conjugates in the presence of different proteolytic enzymes were compared. In addition, the biodegradation of conjugates was investigated in fetal calf serum at 37 °C.

Liposomes were prepared from electroneutral and anionic lipids with a molar fraction of anionic polar groups equal to 0.1. Copolymers of poly-L-lactide (PLA) and polyethylene glycol (PEG) were synthesized via ring opened polymerization of lactide in the presence of PEG, catalyzed by stannous octanoate. The structure and purity of the products were confirmed via NMR spectroscopy, gel chromatography and IR spectroscopy. In aqueous solutions, the copolymers associated thus giving micelles with a hydrophobic PLA core and a hydrophilic PEG shell. The morphology of copolymer micelles was estimated by atomic force microscopy. The average size of PLA particles that were used for constructing MLC was 120-170 nm. A small negative charge was probably imparted due to dissociation of terminal groups of the copolymer. To make negatively charged liposomes interact with anionic PLA particles, they were modified by a biocampatible cationic polymer, polylysine. It was found that ternary PLA-polylysine-liposome complex carries number of liposomes forming multiliposomal container. Liposomes were loaded with different bioactive compounds. It has been shown that the integrity of liposomes in conjugates is retained. The conjugate based on the diblock-copolymer is of particular interest: it demonstrates stability towards dissociation in physiological media. It was shown that conjugates are noncytotoxic and are biodegradable: eventually decompose after being attacked by hydrolytic enzymes within few days. Both conjugates degrade in calf serum down to nano-sized particles within a day. In order to visualize the interaction of liposomal formulations with mammalian carcinoma cells, liposomes were used with their membranes modified by fluorescent labeled lipid. The interaction was detected by using the fluorescence microscopy. It was found that MLC penetrated into the cells, but did not interact with cell nuclei.

The obtained results make multi-liposomal conjugates promising for drug encapsulation and delivery.

Acknowledgements

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COMPOSITES BASED ON SAWDUST AND SOME NEW BINDERS

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During last decade the attention of specialists grows intensively to composites on the basis of wood polymer composites (WPC). Simple technology of manufacture, wide possibility of variation of exploitation properties and recurring processing, ensure low price of these materials.

Our work is devoted to obtaining and investigation of mechanical and thermal properties of composites on the basis of high dispersive and dry sawdust with different organic binders. It was shown that the mechanical strength of composites based on some silicon-organic binders obtained at increasing temperature in the range 90 - 120°C and fixed pressure (15 MPa) monotonically increases in the range 4.5 up to 21 MPa. By mean of the selection of the optimal regime of thermodynamic conditions it is possibility to obtain the composites with sufficient high stable strength at bending and impact viscosity. It was shown that introduction to the composite additionally only 5 wt% of polyethylene leads to formation of composite, the strength of which reaches 22 MPa. Besides of at decreasing of average sizes of the sawdust particles lower than 50 micron this parameter increases up to 33 MPa. This result obviously is described in terms of increasing of integral area of the inter-phase surface between sawdust particles and binders.

In result of investigation of thermal stability of the composites with use of method Vicat it was shown that the composites with enhanced mechanical strength, in general, is in accordance with level of thermal properties (the higher mechanical strength the higher thermal stability).

On the basis of obtained experimental results it is made a conclusion that right selection of composition and technological conditions of obtaining by us WPC is a main way to creation of such materials with high exploitation properties.

Acknowledgments
The financial support of Science & Technology Center in Ukraine (Grant #5892) is acknowledged.

WET- AND DRY-PROCESS FEASIBLE PYRIDYNE-CARBAZOLE TYPE HOSTS FOR PHOSPHORESENT OLEDs

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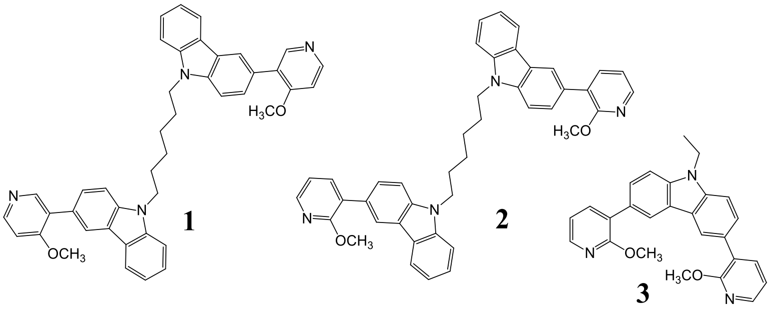
Organic light-emitting diodes (OLEDs) have drawn enormous attention due to their increasing applications in flat-panel displays and solid state lightings[1]. Nowadays, phosphorescent materials become ideal for fabricating high-efficiency OLEDs, because they can theoretically approach a nearly 100% internal quantum efficiency by harvesting singlet and triplet excitons simultaneously through intersystem crossing[2-5].

A wet- and dry-process feasible host material is crucial to realize, respectively, low cost roll-to-roll fabrication of large area and high performance organic light-emitting diodes with precise deposition of organic layers. We demonstrate high efficiency phosphorescent OLED devices by employing a newly synthesized carbazole- based hosts materials: 1,6-bis[3-(2-methoxy-3-pyridinyl)carbazol-9-yl]hexane (**1**), 1,6-bis[3-(6-methoxy-3- pyridinyl)carbazol-9-yl]hexane (**2**) and 3,6-di(2-methoxy-3-pyridinyl)-9- ethylcarbazole (**3**). By doping a typical green emitter *fac* tris(2-phenylpyridine)iridium (Ir(ppy)3) in the compound **1**, for example, the resultant wet-processed device exhibits at 100 cd m-2 a current efficiency of 27 cd A-1 and a power efficiency of 16.1 lm W-1. The dry-processed device shows a current efficiency of 61 cd A-1 and a power efficiency of 62.8 lm W-1. The high efficiency may be attributed to the host possessing an effective host-to-guest energy transfer, effective carrier injection balance, and the device architecture enabling excitons to generate on both host and guest.



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Acknowledgements
This work was financially supported by Ministry of Science and Technology (Taiwan) and by Research Council of Lithuania through the grant number of TAPLLT1/2014.

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AGGERATIVE BEHAVIOR OF BLOCK COPOLYMERS IN THE BULK AND NONSELECTIVE SOLVENTS: AB vs. ABC

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Block copolymers represent a special class of hybrid compounds from chemically dissimilar subchains (blocks), covalently bound into one molecule. Recent developments in polymerization techniques, including controlled radical polymerization, make it possible to unite within single macromolecule various blocks A, B, C, D… of different lengths in practically numerous combinations. Since these blocks are often incompatible and demonstrate a tendency for segregation, a question arises about the structure of these polymer materials in the bulk and in dilute solutions in nonselective solvents; in last case the existence of isolated macromolecules could be anticipated.

To answer this question we have synthesized AB and ABC multiblock copolymers including blocks of poly(tert-butyl acrylate) (PtBA) or poly(arylic acid) (PAA), poly(n-butyl acrylate) (PBA) and polystyrene (PS) in various sequence by means of RAFT-polymerization.[1] Macromolecules contain 2-5 blocks with cumulative polymerization degree of units of each type 30-370. The differential scanning calorimetry shows segregation of chemically dissimilar blocks in the bulk for both AB and ABC types of block copolymers.[2]

The most intriguing was the copolymer behavior in dilute solutions in nonselective solvents, e.g. dimethylformamide (DMF), studied by dynamic light scattering technique. While all kinds of AB (PS-PAA, PS-PBA, PBA-PAA, PS-PtBA, etc.) block copolymers exist as single coils, a strong tendency for aggregation was observed for ABC multiblock copolymers. Aggregates represent themselves some sort of loose intermacromolecular structures with the average hydrodynamic radius 60-120 nm, quite stable towards temperature variations (10 – 60^{o}C). The degree of aggregation can be diminished by selective improvement of solvent quality towards one of the blocks or through decreasing thermodynamic incompatibility of constituent blocks of ABC copolymer.[2]

In general, our investigations have demonstrated that AB block copolymers with two chemically dissimilar blocks segregate in the bulk but could be definitely dispersed up to single macromolecules by dissolving in nonselective solvents. When we add the third block and shift to ABC block copolymers the tendency for block segregation becomes so strong that copolymers form aggregates even in nonselective solvents. There is no doubt that this circumstance should be taken into account while synthesizing, characterizing or processing multiblock copolymers.

Acknowledgements
The Russian Foundation for Basic Research is acknowledged for support under grant No 14-03-00155-a.

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THE INTERACTION OF ANIONIC LIPOSOMES WITH CATIONIC MICROGEL PARTICLES

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Liposomes have long been used as carriers for both hydrophilic substances trapped in an aqueous interior or sorbed by the surface of liposomes and hydrophobic reagents incorporated in a lipid bilayer. In particular liposomes are used for delivery of drugs, contrast agents, fluorescent dyes etc. By assembling of multiply liposomes on a colloidal particle one can considerably increase the efficiency of such delivery systems. Moreover, the liposomes sorbed on the stimuli-responsive microparticles could be used for the control release of the substance trapped into the liposomes.

In this work, the interactions of negatively charged liposomes based on phosphatidylserine and phosphatidylcholine with cationic microgel particles were studied. Microgels with different cross-linking degrees (2 and 4 mol% of cross-linking agent) were synthesized by precipitation copolymerization of N-isopropylacrylamide (NIPAM) and N-(3-aminopropyl)methacrylamide hydrochloride (APMH) (poly(NIPAM-*co*-APMH). The process of binding of anionic liposomes with cationic microgel particles was studied and the amount of liposomes associated with a single microgel particle was estimated. It was shown that liposomes immobilized on the microgel surface maintain their integrity. Due to the presence of thermosensitive comonomer, NIPAM, the microgel particles undergo a sharp volume decrease at the temperatures higher than volume phase transition temperature (VPTT). It was found that at the elevated temperature (T>VPTT), liposome content is released as a result of liposomal membrane destabilization induced by the collapse of microgel particles.

Thus, using liposomes electrostatically adsorbed on the surface of thermosensitive microparticles one can obtain the system in which liposomes are capable to release its content as a respond to the environmental change.

Acknowledgements

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SYNTHESIS OF AMPHIPHILIC BLOCK-COPOLYMERS BASED ON ACRYLIC ACID, N-ISOPROPYL ACRYLAMIDE AND BUTYL ACRYLATE, AND THEIR SELF-ASSEMBLING IN AQUEOUS MEDIA

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Recent developments in controlled radical polymerization techniques make it possible to design macromolecules with definite architectures. Among possible structures, block-copolymers attract increasing interest due to combination of properties of different polymers in one product and due to microphase segregation observed in bulk and in dilute solutions in selective solvents.

When amphiphilic block copolymers are considered, the possibilities to govern their self-organization increase. It comes from incorporation of pH and thermal-sensitive blocks in hydrophilic part of block-copolymer and varying the length of hydrophilic and hydrophobic blocks. Up to the present time, numerous amphiphilic block-copolymers have been synthesized using techniques of controlled radical, living anionic or group transfer polymerizations and their morphologies have been described.

Here we suggest new type of amphiphilic block polymer, which contains units of pH-sensitive acrylic acid, thermal sensitive N-isopropyl acrylamide and hydrophobic n-butyl acrylate.

RAFT copolymerization of acrylic acid and N-isopropyl acrylamide was studied in 1,4-dioxane in the presence of dibenzyl trithiocarbonate as RAFT agent at various monomer compositions. In all the cases copolymerization proceeded via the living mechanism and resulted in the formation of narrow dispersed copolymers.

Synthesized random copolymers as well as triblock copolymer poly(acylic acid)-block-poly(N-isopropyl acrylamide)-block-poly(acrylic acid) were used as polymeric RAFT agents in butyl acrylate polymerization in DMF. Independently from the chemical structure of polymeric RAFT agent the block copolymers were formed. Their molecular weight increased with the monomer conversion.

The block copolymers obtained at limited conversions were dissolved in DMF, and then they were subjected to dialysis first against alkaline water, and then against pure water. As a result, block copolymer dispersions in water were obtained. The study by dynamic light scattering revealed that these dispersions are characterized by narrow particle size distribution. The average hydrodynamic radius of the particles was governed by changing pH and the temperature.

Acknowledgements

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INFLUENCE OF FABRIC STRUCTURE ON LOADING CAPABILITY OF TERRY FABRICS FINISHED WITH MICROCAPSULES

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Microencapsulation technology has attracted more attention with the development of new functional textile with magical effects [1]. It was observed a decreasing tendency in the number of microcapsules (MC) that remain on the fabric when the number of washing cycles increases [2]. Besides, the textile structure was found to be the important factor affecting microencapsulation [3]. Studies [4, 5] deal with the effect of binder types and binding conditions on the durability of microencapsulated textile. However, there have been only single efforts to apply microcapsules on terry textile as well as to explore the relationship between weaving parameters and loading capability of MC. Meanwhile, such analysis can aid researchers with chemical background to select suitable MC procedures.

In this study, the aroma agent containing Eucalyptus essential oil for cosmetic, well-being, and health enriching benefits was used for the development of ramie-cotton terry fabrics using impregnation (drying at 105-110 °C (for 1 min), thermo-fixing at 150 °C temperature (for 2 min), MC – 30 g/L, binder concentration – 80 g/L). The research was carried out to evaluate the performance of microencapsulation effect and loading capability on ramie and cotton yarns as well as on terry woven fabrics (pile warp: 67 tex, ground warp: 25 tex x 2, ground weft: 50 tex) with regard to weft density (8-16 cm^{-1}). By SEM analysis it was confirmed that microcapsules were fixed on ramie and cotton yarns as well as on terry textile (Fig. 1); the loading capability was 3.8, 11.7 and 12.5-23.1 %, respectively.

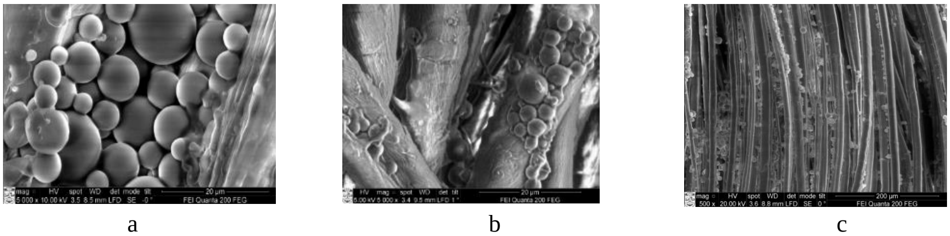
a b c

Fig. 1. SEM micrographs: a - ramie yarns (5000 x), b - cotton yarns (5000 x), c - loop cover of terry fabric (500 x).

Based on the obtained experimental results, it can be concluded that due to the specific structure of terry fabric which characterized by high porosity, bulkness, fullness in volume the add-on of terry fabrics with various weft density was in 0.8-8.7 % and in 11.4-19.3 % higher compared to add-on of investigated ramie and cotton yarns, respectively.

The terry fabrics with microcapsules may find numerous applications and be an attractive process for development of functional innovative products for home textile, bath-room and sauna textile, clothing as well as for hygiene articles because of imparting longer lasting effect and being more environmental friendly than other chemical treatments.

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TWIN COMPOUNDS WITH PHENYLETHENYL SUBSTITUTED INDOLES AS EFFICIENT ELECTROACTIVE MATERIALS FOR CHARGE TRANSPORTING LAYERS

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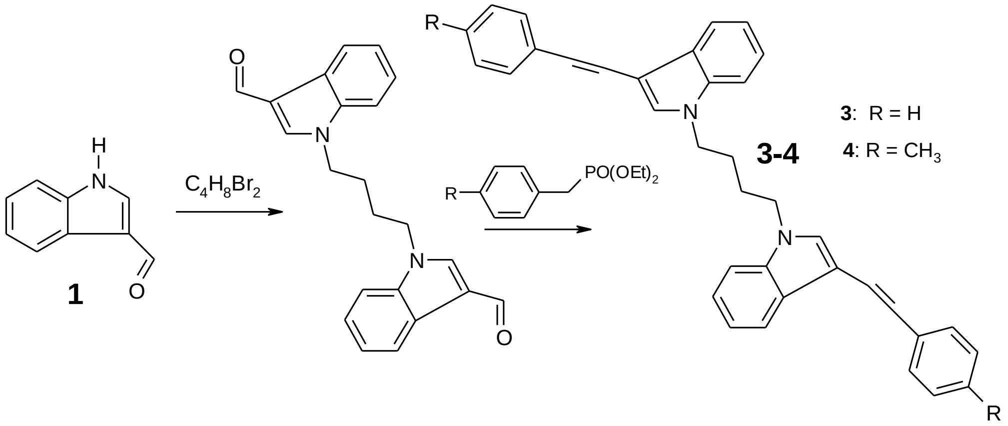
The main approach that has been employed to improve efficiency of organic light emitting diodes (OLEDs) is the formation of an additional hole transporting layer (HTL) in the multilayer devices [1, 2]. We will present in the conference new hole transporting materials and their application in OLED devices.

The synthesis of twin derivatives (**3-4**) containing 2-phenylvinyl substituted indole rings was carried out by the synthetic route shown below. Commercially available indole-3-carboxaldehyde (**1**) was firstly used for the preparation of 1,4-di(3-formylindol-1-yl)butane (**2**) by the earlier described procedure [3]. The objective twin derivatives **3-4** were prepared by reaction of the formylindol-1-yl-containing dimer **2** with an excess of diethyl benzylphosphonate or diethyl 4-methylbenzylphosphonate, correspondingly. The synthesized compounds were identified by mass spectrometry and ^{1}H NMR spectroscopy.



To investigate the hole-transporting properties of the materials, OLED devices were fabricated with a device configuration of ITO/HTL of **3** or **4**/Alq$_3$/LiF/Al. In this device configuration thin layer of **3- 4** were used as HTL materials, Alq$_3$ was used both as a light emitting and electron transporting material, ITO and LiF/Al were used as an anode and cathode, respectively. Among these OLEDs, the device containing hole transporting material **3** demonstrated the best overall performance, i.e. turn on voltage of 4.4 V, maximum brightness of 3400 cd/m^2 and maximal photometric efficiency of 2.75 cd/A.

Acknowledgement

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INTERACTIONS BETWEEN ADDITIVES IN THE COMPOSITE TAPE YARNS

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The object of research is the interaction of additives used in the production of composite tape yarns for functional woven packaging materials. Yarns produced by extrusion of polypropylene (PP) and functional additives are analysed. The interaction of additives Granic 422 (additive A) (GCR Group Co., Spain) and Polycom JB 7100 (additive B) (Omega Plasto Compounds Co., India) is analysed by varying the percentages by weight of additives in the yarn (x_1 ir x_2) in the interval of 0.0 – 8.0 wt% (Fig. 1).

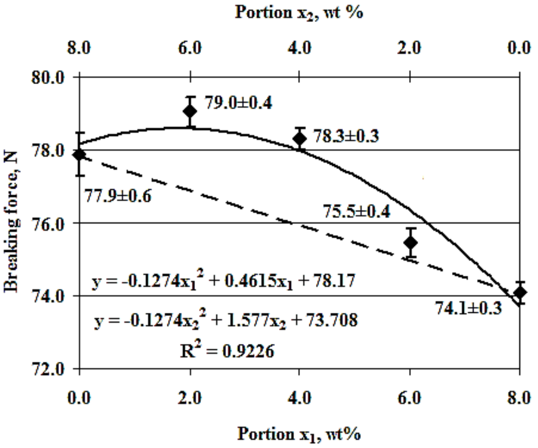

Fig. 1. Impact of the percentage of additives (x_1, x_2) on the breaking force of composite tape yarns: x_1 – Granic 422; x_2 – Polycom JB 7100. The solid line is the result meaning that the interaction between additives exists, the dotted line – the result when there is no interaction between additives.

The morphological, geometrical and mechanical properties of the yarns were investigated. The following yarn indicators are analysed: thickness, width, linear density, breaking force, tenacity, elongation at break, specific work of break, initial modulus. The statistical significance of the difference between the results without additives and the case when this interaction exists was tested with the Student criterion. The scanning electron microscopy (SEM) sample surface images were analyzed using IMAGE J software (National Institute of Health, USA). The number of particles visible in the surface area of 10,000 μm^2 of test samples, and the average particle area was determined. It was found that the sample with additive A has 35.7%, while with additive B has 25.0% less particulate matter compared with a sample containing 4.0 wt% of each of the two additives. The average particle area of the sample with additive A is 0.222 μm^2 and with additive B – 0.198 μm^2. When 4.0 wt% of both A and B additives were used, the average particle area was 0.039 μm^2. Under the interaction of additives, the statistically significant linear density increase was obtained. In addition, smaller particles of additives result in smaller cracks on the surface of the yarn. Both of these reasons lead to the higher breaking force indicator. It was found that with simultaneous use of the additives A or B (x_1= 2.0 wt% or 4.0 wt%; x_2= 6.0 wt% or 4.0 wt%), the breaking force is higher relative to the yarn variants where there is no interaction between these additives (Fig. 1). Significant influence of the interaction of additives was obtained also in terms of other indicators.

MICROCRYSTALLINE CELLULOSE FILLERS IN COMPOSITES WITH POLYETHYLENE AND LIGNIN

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Cellulose fibres and lignocellulosic materials recently have aroused considerable interest in their use as fillers in thermoplastic materials. These fillers are biodegradable, bio-based, exhibit a low density, have a low cost and are the basis for the development of wasteless production.

In this work, microcrystalline cellulose (MCC) fillers were obtained for their use in composites with polyethylene, lignin and a coupling agent.

The MCC fillers were obtained from bleached softwood and hardwood kraft pulp and cotton fibres. The raw materials were treated using a thermocatalytic destruction method developed at the Cellulose Laboratory of the Latvian State Institute of Wood Chemistry. In compliance with this method, the raw material was impregnated with week hydrochloric acid solution (0.02-0.1%) and then thermally treated at elevated temperatures (70-120ºC). The destructed material was ground in a ball mill. The treatment conditions were developed for each raw material, and MCC powder samples were obtained, which contained microparticles with different shape and size. Composite samples, containing high density polyethylene, 50 wt% of softwood kraft lignin, 20 wt% of MCC and a coupling agent, were produced. The mechanical properties of the obtained samples were investigated. It was established that the mechanical properties of composites were improved to a greater extent by the MCC filler obtained from cotton fibres. This can be connected with the fact that the cotton MCC powder contains fibre fragments with a higher aspect ratio (reaching 30), and the single fibres are stiffer and stronger due to the higher degree of crystallinity. At a 20% filler content, the tensile strength, modulus of elasticity, notched Charpy impact strength and unnotched Charpy impact strength of composites with the MCC filler obtained from cotton fibres increase by 30, 64, 50 and 15%, respectively, and elongation of break decreases by 20%. The MCC filler obtained from hardwood (birch) kraft pulp at the hydrochloric acid concentration and treatment temperature, which correspond to the destruction of wood pulp to a DP of 500-600 (aspect ratio reaches 10) also sufficiently improves the mechanical properties of composites. In this case, at a 20% filler content, tensile strength, modulus of elasticity, notched Charpy impact strength and unnotched Charpy impact strength increase by 32, 51, 60 and 14%, respectively, whereas elongation at break does not change. The MCC fillers from hardwood and softwood pulp, obtained in thermocatalytic treatment conditions leading to the levelling-off degree of polymerization (LODP) of 300-400, improve the mechanical properties of composites to a smaller extent. Therefore, the obtained MCC fillers can be used in composites with polyethylene and lignin to improve their mechanical properties.

Acknowledgements

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LAYERED COMPOSITE MEMBRANES BASED ON SULFONATED POLY(PHENYLENE OXIDES) AND CONDUCTING POLYMERS

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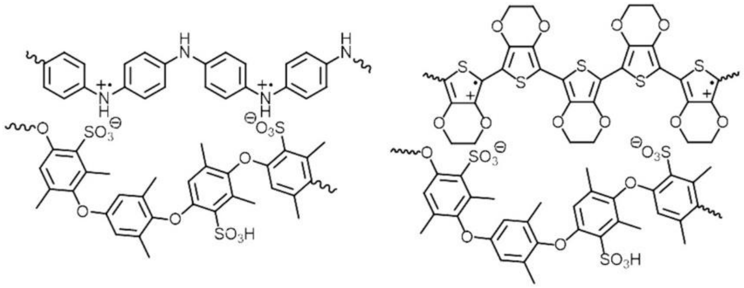
Mixed ionic-/electronic- conducting materials are widely used in Li-ion batteries, electrochromic smart windows and other electrochemical devices. Polymer-based mixed conducting membranes have received especial recognition due to their easy preparation and good mechanical characteristics [1,2].

In the present work, novel mixed conducting polymer membranes based on ion-conducting sulfonated poly(phenylene oxides) films (SPPO) and electrically conducting polymers (polyaniline and poly3,4-ethylenedioxythiophene) were developed.



Composite membranes were obtained by oxidative polymerization of aniline or 3,4-ethylenedioxythiophene in the presence of template SPPO membranes. For this purpose, free-standing membranes of SPPO of various sulfonation degrees (0–60%) were first swollen in aqueous solutions of monomers and then treated with ionic oxidant (ammonium persulfate).

It was found that SPPO membranes acted as templates accelerating the polymerization. Polymerization proceeded presumably interfacially resulting in formation of continuous layers of conducting polymer (0.1 to 7 μm-thick) on both sides of the template SPPO membranes. Increase in monomer concentration, polymerization time, or sulfonation degree of SPPO led to the growth of the thickness of conducting polymer layers. Prepared composite membranes had proton conductivities of 0–0.04 S/cm and in-plane electrical conductivities of 0.0001–0.2 S/cm. Increase in thickness of conducting polymer layers increased in-plane electrical conductivity of composite membranes, decreased their through-plane proton conductivity and permeability to methanol and VO^{2+} ions.

Acknowledgements
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MODIFICATION OF KRAFT LIGNIN BY EPICHLORHYDRIN IN THE PRESENCE OF ALKALI CATALYST AND EVALUATION OF CHARACTERISTICS OF MACROMONOMERS OBTAINED

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Cured epoxy resins are thermosetting heat-stable polymers with high mechanical properties and chemical resistance. The coatings, adhesives and reinforced composites on the basis of epoxy resins are widely used in many industrial applications including electrical, electronic appliances, automobile industry etc.

Bisphenol-A obtained from fossil resources is used as a precursor for most commercial epoxy resins. Bisphenol-A are responsible for numerous favorable properties of final material, but unfortunately it reveals estrogenic activity and, therefore, is referred to as an environmental hormone. Therefore, it is necessary to find an alternative material for epoxy resins synthesis [1,2]. Besides that, utilization of renewable biomass resources for polymers and chemicals has drawn increasing attention worldwide.

Lignin is one of the main compounds of lignocellulosic biomass, which constitutes 15-35% of plant material. Lignin is a three-dimensional amorphous biopolymer formed by three major monolignols (p-coumaryl, coniferyl and sinapyl alcohols) with different ratios, linked together by various types of ether and carbon-carbon bonds. The aromatic structure of lignin and presence of phenolic hydroxyl groups make lignin as an attractive bisphenol-A substituent, able to modification via reaction with epichlorhydrin.

In this work commercial kraft lignin LignoBoost^{TM} was epoxized in dimethylsulfoxide media, using epichlorhydrin and potassium hydroxide as reagents for two steps lignin glycidylation. The influence of molar ratio of lignin, epichlorhydrin and potassium hydroxide in initial reaction mixture on the extent of lignin epoxidation and structure of macromonomers obtained was studied by means of FT-IR spectroscopy, DSC, SEC and wet chemistry methods.

Acknowledgements

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SOME FUNCTIONAL PROPERTIES OF COMPOSITE MATERIAL FROM RECYCLED TIRES AND POLYURETHANE BINDER.

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Production of composite material is considered as one of the most perspective directions of scrap tires reuse in combination with polymer binder [1-2]. In our previous studies optimization of composition and technology of the production of composite material from mechanically grinded scrap tires and polyurethane type binder were carried out [3]. It was also established, that mechanical properties of the composite material are strongly dependent not only on the composition of material and the reactivity of polymer binder, but also on technological parameters (molding pressure, temperature) and environmental conditions (relative air humidity RH) [4].

The present research is as a continuation of the authors' previous research of composite material and practical application of composite material largely connected with water. The aim of present study was to estabilish certain functional properties of the material in water medium. Water permeability, absorption and swelling of the composite material after being exposed to water for certain period were determined.

Water absorption, permeability and swelling of the composite material showed close correlation with polymer reactivity. The results show that permeability of samples decreases with an increase of polydispersity of the rubber crumb and polymer binder content. This can possibly be explained by the reducion of voids and therefore the formation of a more compact structure of the composite material.

The correlation between the swelling degree of composite material, the polymer binder content and reactivity of polymer used in composite material as well as the formation temperature has been studied. It was observed, that not only the reactivity of the selected polymer binder, but also the potential of obtaining a more compact structure by increasing the binder functionality and content in the material is responsible for the suggested correlations.

A direct influence of the formation temperature on the swelling degree was demonstrated. The swelling degree is higher for samples produced at T=40°C. It can be explained with a direct influence of higher formation temperature on a higher crosslinking degree of polymer and therefore the swelling properties of the material. It is also closely correlate with the results of the previously conducted studies regarding the investigation of Shore hardness of similar samples produced at different temperatures [5]. Molding pressure, temperature and the distribution of rubber particle sizes also demonstrate a direct influence on the water absorption and permeability of the composite material.

The obtained results are useful for the practical application of selected composite material with desirable and predictable functional properties.

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SALICYLATE POLY(IONIC LIQUID)S AS UNIQUE DRUG DELIVERY SYSTEMS

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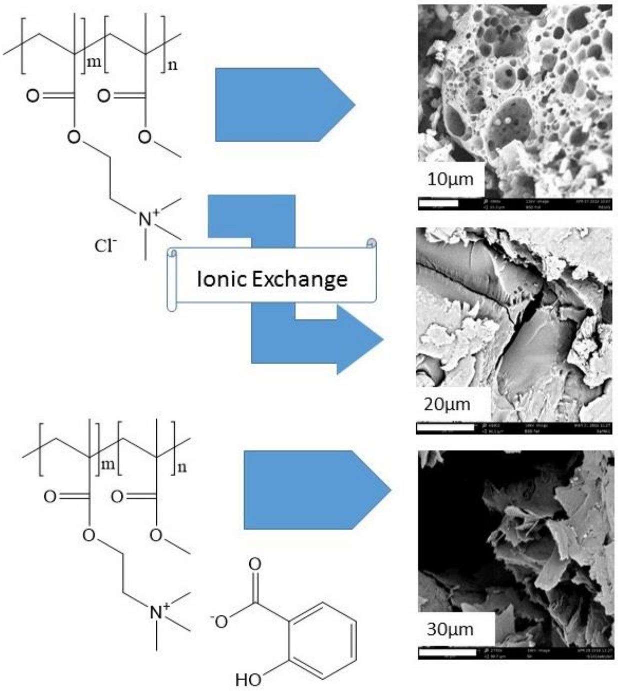
Poly(ionic liquid)s are interesting group of macromolecules that have many applications. The synthesis of compounds of this type is possible both by conventional radical polymerization, ionic polymerizations or controlled radical polymerizations[1]. Properties of obtained products can be next tuned by ionic exchange[2]. Thus it creates novel way to design drug carriers.

The well-defined salicylate anion (Sal$^-$) containing copolymers have been synthesized on both ways, that is direct synthesis from (N,N,N-trimethylammonium)ethyl methacrylate salicylate monomer and by ionic exchange on chloride anion (Cl$^-$) in analogous ionic polymethacrylates.



Obtained products have been compared for properties and subjected for SEM, NMR, FT-IR and DLS analysis to confirm their morphologies, structures and usefulness as drug carriers.

Acknowledgements

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MODIFICATION OF LIGNOCELLULOSIC FIBERS AS A RESULT OF MECHANOCHEMICAL CONVERSIONS

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Nowadays, the solid-phase chemical processes initiated by mechanical action are receiving much attention for modification of polymers, because they are more environmentally friendly and cost-effective compared with the existing ones. In contrast to classical methods, in which heat energy is needed for initiating reactions, the mechanochemical approach allows an essential reduction in energy consumption and carrying out modification in a much shorter time, using compact reaction facilities [1-2]. In the work, we modified lignocelluloses fibres – hardwood residue of wood mechanical processing, using high energy ball milling with a rotational speed of 300-600 r.p.m. and modification time of 0.5-3 h at room temperature. During the milling, the fibers underwent the action of the reaction mixture in the presence of the oxidation-reduction system. The mechanochemical action was carried out in a planetary mill "Retsch ". Balls of diameter 10 mm made from ZrO steel were used as a milling means. The reaction mechanism for such a type of modification consisted of a complex set of consecutive and competitive reactions, having both oxidative destructive and polymerization / polycondensation character. With lignocellulosic matrix degradation and decreasing amount of ether bonds and OH-groups, the formation of new C-O, C-N and C-C bonds was observed. The results showed that, depending on the modification parameters, the modified products' yield ranged from 62% to 99%, and the lignin, cellulose and hemicelluloses content in the products varied in the range of 19.5-33.9%, 44.1-57.2% and 16.7-22.5%, respectively. The modified lignocellulosic particles had a more condensed structure than the initial ones due to the proceeding pronounced polymerization and polycondensation processes. In this connection, with increasing rotational speed and modification time, the yield of the wood microparticles <100 mkm after milling remarkably decreased.

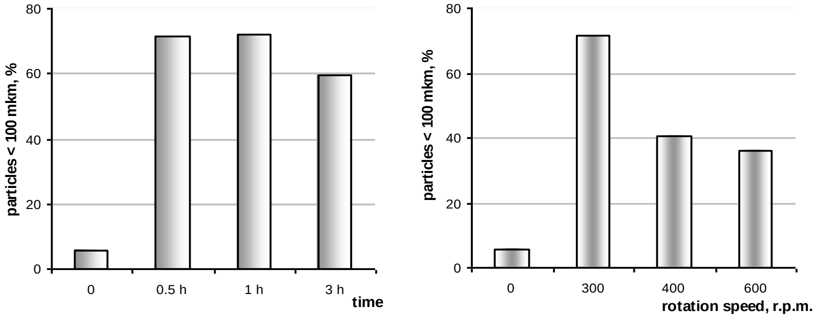

Fig. 1. Dependence of the rotational speed and time on the yield of the modified particles < 100 mkm

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NAPHTYL OR PYRENYL SUBSTITUTED 2-PHENYLCARBAZOLES AS HOLE TRANSPORTING MATERIALS FOR ORGANIC LIGHT-EMITTING DIODES

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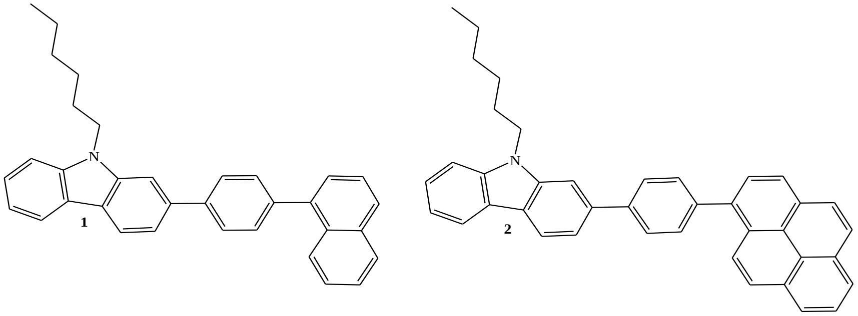
Organic light-emitting diode (OLED) displays are emerging as the mainstream of next-generation display due to their superior performance and flexibility. Hole transport materials (HTMs) for PhOLEDs have several requirements including high triplet energy for triplet exciton confining, adequate energy level of the highest occupied molecular orbital (HOMO) for effective hole injection, as well as high hole mobility [1, 2, 3]. A new series of carbazole-based compounds **1-2** aiming to facilitate hole transport function in OLEDs were synthesized and characterized (Scheme 1).



Scheme 1. Structures of compounds **1** and **2**

The glass transition temperatures of **1** and **2** were estimated to be 58 and 61℃, which can provide morphologically-stable films for EL applications. Compound **2** possesses an adequate ionization potential and triplet energy gap of 5.54 eV and 2.48 eV, respectively, which makes **2** a suitable HTM for use in red phosphorescent OLEDs. In contrast, a rather higher ionization potential of **1** was estimated to be 5.72 eV, thus the p-type conducting dopant should be introduced in device fabrication. The EL characteristics of the tested devices indicated that devices with compounds **1** and **2** exhibited performance comparable to that of NPB-based devices. By introducing the p-type dopant, the respective peak efficiencies of red phosphorescent OLEDs with compounds **1** and **2** were respectively recorded at 15.4 % (26.0 cd/A and 24.2 lm/W) and 17.3 % (26.1 cd/A and 19.1 lm/W). The excellent results of these devices with the new carbazole-based compounds indicate a new path of molecular designs for HTMs.

Acknowledgements
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THERMAL RESISTANCE OF LEATHER MODIFED BY MONTMORRILONITE DISPERSIONS

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Chrome tanning plays an important role in stabilizing the collagen derma structure in leather production. The high performance properties of leather, resistance against high temperatures, chemical materials, soaking are ensured by the stabilizing and structuring action of various tanning materials on derma collagen. The particles of modified montmorillonite and chromium compounds are reported to produce strong chemical bonding with the derma collagen. Montmorillonite falls under the group of minerals with high dispersion and ability to absorb anions and cations. As a result of modification, dispersions of montmorillonite may acquire the necessary colloidal-chemical properties in terms of effective diffusion with chromium complexes and active centers of derma collagen [1, 2].

The aim was to investigate thermal resistance of leather and to analyze physical and chemical transformations of derma collagen structure against temperature.

To determine thermal resistance of leather samples, first, they were tanned with chromium oxide (1,5 % Cr_2O_3) and a combined action of chromium oxide (1,0 % Cr_2O_3) and chromium modified dispersions of montmorillonite (0,25 % Cr_2O_3 and 2,5 % mineral). 100 mg leather samples were used for investigation. The thermal analysis was performed in a dynamic mode in the air under continuous heating from 20 to 800 °C with the temperature increase rate 10°C per minute.

The investigation shows that the leather structure affected by high temperature undergoes several changes including vaporization of absorption water, melting of a protein component, loss of crystalized water and thermal oxidizing, which ends with the disintegration of carbon frame and extraction of coke mass.

The thermal investigations showed different thermal resistance for chromium montmorillonite tanned leathers and for those tanned with chromium compounds only. The differences manifest in a different starting temperature of thermal oxidative degradation, weight loss rate and the level of activation of thermal destruction process at various stages.

The decreased thermal destruction rate and increased energy consumption are observed for the leather tanning with modified dispersions of montmorillonite, which is the evidence of the high stabilizing and structuring action of mineral dispersions on derma collagen. It has been proven that the use of modified dispersions of montmorillonite for leather tanning allows to increase thermal resistance of leathers versus chromium tanning process by 9–14 % and the cumulative thermal effect by 6–9 % with the decreased consumption of chromium compounds for leather tanning by 17–20 %.

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THE PROPERTIES OF REINFORCED NONWOVEN COMPOSITES

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The use of removable crop materials, such as hemp, in various applications offer economic and social benefits in different industries due to rural economies through new agriculture markets for farmers and associated industries also with appreciation of petroleum- based materials prices as well as customs and government legislation attitude for eco-friendly materials [1]. Fibre-reinforced thermoplastic matrix composites have gained commercial success in the semi structural and structural applications due to the low production cycle and processing cost [2].

In our experiment a series of non-woven (NW) composites are made from a fibrous blend of hemp and thermoplastic fibres reinforced with thermoplastic sieve by compressing method. The mechanical properties, water penetration and air permeability of produced composites are investigated.

For NW web production the local hemp fibres variety “Bialobrzeskie” of Kraslava district (designation HA; length 50-60±2 mm) pre-treated with sodium hydroxide, recycled polyethylene terephthalate fibres (PET; length 60±2 mm) and polypropylene fibres (PP; length 20±2 mm) are used.

The NW web is made with laboratory carding machine (337A MESDAN) from fibrous blend (HA- 81%, PET- 13% and PP- 6%) and the samples (160 x160 mm) are cut out and two mass NW with a sieve on one side or both sides of web are produced on laboratory press (LP-S-50/S ASTM) with pressure 25±2 kN at 140± 2 °C temperature.

The NW surface parameters are calculated according LVS EN ISO 139:2005. For testing of NW mechanical properties Zwick Universal testing machine, according LVS EN ISO 13934-1-2001 is used. For determination of NW resistance to water penetration hydrostatic pressure test according LVS EN ISO 9073-16:2009 and for air permeability EN ISO 9237:1998 is applied.

Produced NW thickness (0.64-0.83 mm) and mass (90-124 g/m^2) depends on web initial mass (1.89±0.01g and 2.57±0.01g). The influence of sieve disposition (one side or both sides) on tensile strength – elongation characteristics is significant. The water penetration of NW is within the limit 15-22 mm/s and the air permeability (13-25 L/min).

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WASTEWATER WOOD BIOMASS AND ITS PRACTICAL APPLICATION

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The production of veneer in Latvia and in many counties of East Europe is realized by the hydrothermal treatment of hardwood in special water basins for 16–18 h at 50–60°C and normal pressure. The obtained wastewater contains lignocellulosic biomass, consisting of hemicelluloses, lignin, lignin-hemicelluloses complexes and wood extractive substances. In recent years, the coagulation–flocculation method with the use of cationic polyelectrolytes (polyethylenimine, polydiallyldimethyl-ammonium chloride, chitosan, etc.) has been widely used for wastewater treatment [1]. The aim of this work was to increase the efficiency of the recovery of birch biomass from plywood production wastewater using a new developed composite coagulant, and to study the possibility of using the extracted biomass for dusty soil aggregation.

The developed composite coagulant presented colloid nanosized particles of a metal-polymeric complex, containing a salt of polyvalent metal and high molecular brunched polyethylenimine (PEI). The polymer-colloid complex was formed due to the donor-acceptor interactions between imine atoms and metal cations. Besides, the complex was stabilized by H-linkages, taking into account the hydration shell around the metal ions. The effect of the dosage of the composite coagulant, pH values and temperature of the recovery process on the efficiency of the biomass separation from a model solution, imitating the industrial wastewater, was studied. At the optimal technological parameters, the recovery of the wood biomass achieved 97%, but the extraction of lignin and lignin-like substances was more than 65%. Due to the polymeric and polyfunctional nature, the recovered wood biomass has glue properties. It is known that the dust at the surface of unpaved roads creates environmental problems. In this connection, the separated biomass was tested as a structuring agent for dusty soils. It is found that, with increasing its amount in the soil, the content of large sandy aggregates > 1 mm increases (Fig. 1.) that will promote the decrease of soil blowing off from the road surface.

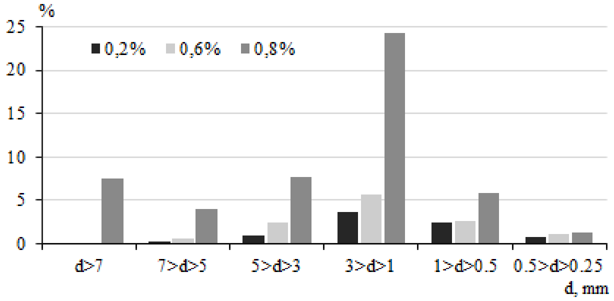

Fig. 1. Fractional composition of sand structured with separated biomass

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INVESTIGATION AND OPTIMIZATION OF COATING COMPOSITION FOR LEATHER DRESSING

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The modern dressing of semi-finished leather implies insuring a set of properties of coating and finished leather, which has to meet process, operational and aesthetic requirements and to ensure comfort and long use of leather products. The use of new efficient dressing materials allows to obtain leather coating with desired properties depending on purpose of products and consumers' requirements.

The objective of the investigation was to explore the properties of the modified acryl/urethane coating composition, the resulting polymer films, and its optimization.

The study used soft acrylic Saracryl, hard urethane PUR 2125 film binders as well as EPAA and Basic Chromium Sulfate (BCS) products. EPAA helps improve performance characteristics of coating films [1]. To improve water resistance of coating films, the BCS was introduced to the coating composition, which allowed to significantly reduce swelling of the subject polymer materials in water [2]. An individual influence of the products on film binders and their complex impact on the f acryl/urethane mix was identified.

An increase of EPAA content in polymer films increases their elasticity modulus and ultimate tensile strength, thus demonstrating the structuring effect. This is also demonstrated by the nature of the tensile elongation at break curve, which gradually drops with EPAA concentration increase.

The supplementary treatment of Saracryl + EPAA binders by BCS in the amount of 1% of EPAA mass proves the enhanced structuring effect and further film strengthening, which is reflected in the physical/mechanic curves. The treatment of Saracryl + Sarpur + EPAA binders with BCS in the amount of 1% of EPAA mass produces further film strengthening, which is reflected in the physical/mechanic curves.

The analysis of polymer film swelling shows that additional treatment of polymer films with BCS improves their water resistance (swelling drops 4 times), probably, due to formation of additional physical/chemical bonds between the bonding agent, BCS and EPAA.

A multi-criteria optimization of the developed coating composition with the use of D-optimum simplex-lattice design under Kiefer was done. The following of components ratio was obtained: EPAA – 2,6-2,8, acrylate resins – 43,4 polyurethane – 54. This system will ensure the indices at the following level: elasticity modulus - 1,68 MPa; critical stability - 6,22 MPa; relative elongation - 833 %.

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COATED COTTON FLAME RETARDANCY

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Today textiles' reaction to fire is still a major problem. Its reduction is relevant to all - everyday, technical and special-purpose textiles because these materials are flammable and create a fire hazard. Flame retardants that reduce the spread of flames or inhibit combustion of the material have been developed. [1, 2]

The aim of this study is to research fire reduction in cellulose fibers - plain weave cotton fabric.

Plain weave bleached cotton fabric was used in the experiment. Textile was treated with flame retardant phosphonate Itoflam PES via impregnation method - the optimum concentration of 140 g/L, together with the alkaline agent of 25% NH_4OH - concentration of 60 g/L. Impregnated samples were dried at 120°C for 2 min and heat treated at 180°C for 1 min. Then through application of mesh templates impregnated cotton fabric was coated with different composition continuous coating using industrial printing paste with fire retardant Sb_2O_3 additive produced by CHT BEZEMA. Textile was dried at 100°C for 2 min and thermally treated for 5 min at 150°C. Samples' flammability testing was based on the LVS EN ISO 15025:2003 method. Horizontal-fire test was carried out on both the right and left sides of the textiles. LVS EN ISO 13934-:1999 standard was used for determination of samples physico/mechanical properties. Taber Rotary Platform abraser, according LVS EN ISO 5470-1:2001 was used for detecting textiles' wear resistance.

Preparation Itoflam PES reduces cotton fabric reaction to fire and promotes flame extinction. Continuous coating with print pastes (two of them are with foaming effect) Printperfect LAC 60, Tubiscreen EX-TS and Printperfect EX-AR together with a flame retardant Sb_2O_3, colored with pigments also form a visually beautiful effect and make fabrics flame resistant. Depending on the intended use, best suitable coating can be chosen. Foamed coating that produces 3D effect and is non-combustible could be widely used in interior products, where fire safety is of utmost importance. Different materials whose physico/mechanical properties are important were tested for their tensile strength.

Fabric impregnated with Itoflam PES with extra fireproofing coating reduces cotton's reaction to fire. The resulting effect varies with the type and composition of coating. Thickness of coating has little impact on cotton's fire reaction readings.

The best fire suppression for non foam coating is achieved by paste Printperfect LAC 60, but for foam coating – paste Printperfect EX–AR.

Coatings cause slight increase of tensile strength and decrease of relative elongation. Paste Tubiscreen EX-TS provides the greatest friction resistance, amounting to 3856 abrasion cycles.

Foam finishing has higher abrasion resistance than non foam coatings.

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SYNTHESIS AND PROPERTIES OF PHENANTHROIMIDAZOLE-BASED SELF-POLYMERIZABLE MONOMERS

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Blue organic light-emitting materials have attracted much attention because of their significant applications in flat-panel displays and solid-state lighting.[1] Recently, aryl-substituted phenanthroimidazoles (APIs) have attracted tremendous attention as efficient blue-emitting building blocks due to their simple synthesis, excellent thermal properties, high fluorescence quantum yields, and "bipolar" properties.[2–7]

In this presentation we report on the synthesis and properties of phenanthroimidazole-based self-polymerizable monomers. Structures of monomers **M1-M6** is outlined in **Fig. 1.**

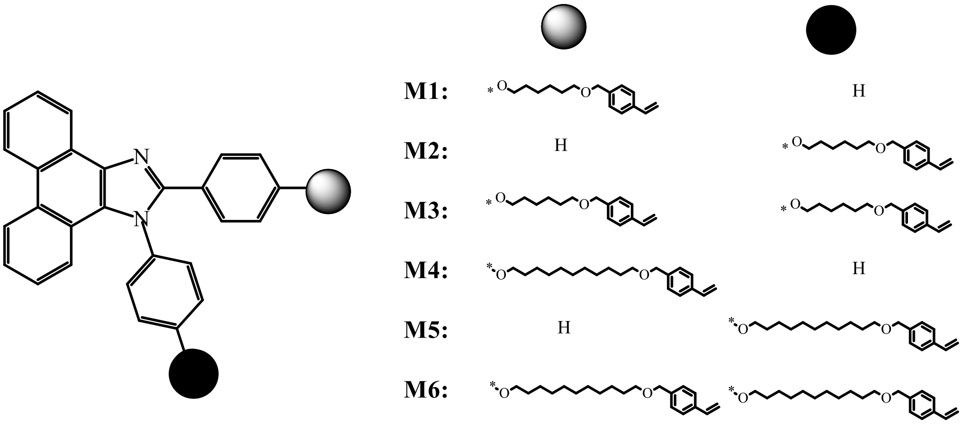

Fig. 1. Structures of phenanthroimidazole-based monomers

The structures of the synthesized monomers **M1-M6** were confirmed by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and mass spectrometry. The thermal properties of monomer were investigated by the differential scanning calorimetry. Optical and photophysical properties were studied by UV and fluorescence spectroscopies. The polymerization kinetics was investigated by DSC and real time FT-IR technique.

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AQUEOUS SOLUTIONS PROPERTIES OF STATISTICAL AND BLOCK COPOLYMERS OF ACRYLIC ACID AND BUTYL ACRYLATE OBTAINED VIA RAFT POLYMERIZATION

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Nowadays the methods of controlled radical polymerization (CRP) give a unique opportunity to explore influence of polymers chains microstructure on their properties. In this study copolymers of acrylic acid (AA) and butyl acrylate (BA) containing 10 mol.% of BA, called "ancor units" due to their ability to adsorb at the interfaces, e.g. "aqueous solution-air", have been investigated. RAFT technique of CRP has allowed to synthesize of precisely identical by composition and molecular mass characteristics (M_n=9400, M_w/M_n=1.17-1.18) AA-BA copolymers varying only in BA units distribution type: statistical and triblock copolymers (with inner poly(AA) sequence). Earlier it was found [1] the strong effect of chain microstructure on the surface tension of poly(AA-BA) aqueous solutions. Here the influence of microstructure on hydrodynamic properties of such copolymers is discussed (Fig. 1).

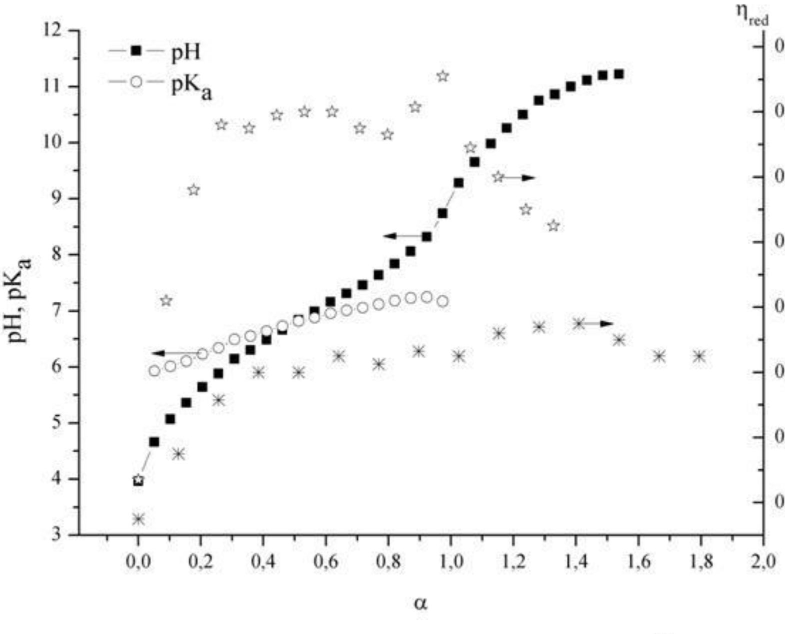

Fig. 1. The dependence of pH, pK_a and reduced viscosity (η_{red}) of statistical (✳) and block (☆) poly(AA-BA) on the degree of neutralization (α). (α>1 indicates the excess of neutralization agent).

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SYNTHESIS BY RAFT AND PROPERTIES STUDY OF RANDOM AND DIBLOCK BOTTLE-BRUSH POLYELECTROLYTES

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Synthetic block-type bottle-brush polyelectrolytes (PE) combine 3 different classes of materials – polyelectrolytes, block copolymers and surfactants. Therefore, they possess unique properties, form stimuli-responsive structures of various topology and have potential applications in biomimetic field [1, 2]. Bottle-brush polyelectrolytes can be synthesized via 3 main strategies: „*grafting-onto*“, „*grafting-from*“ and „*grafting-through*“. Using the second approach, side chains of brush polyelectrolytes can be synthesized by RAFT polymerization of an ionogenic monomer from a backbone containing multiple RAFT chain transfer agent (CTA) groups.

The backbone of the brush polyelectrolytes was synthesized by RAFT polymerization of styrene and vinyl benzyl chloride (VBC). VBC units in the copolymers were modified attaching butylthiocarbonothioylthio moieties [3]. The degree of substitution of VBC units determined by ^{1}H NMR spectroscopy was ranging from 50% to 75%. Polymerization of acrylic acid (AA) from polystyrenic backbone carrying multiple RAFT CTA groups was carried out in dry DO by the method described in our previous work [4]. Molecular weight of the brush polyelectrolytes was rather high, and DP of the side chains varied from 20 to 60. These results are in good agreement with theoretical predictions. Diluted solutions (0.05 w/v %) of random and diblock bottle-brush PE in dry DO and DMF containing 2%, 10% and 20% of water were studied by DLS. DLS measurements were done at various temperatures (25ºC, 30ºC and 40ºC). Since water is non-solvent for hydrophobic backbone and a good solvent for the side chains of pAA, the polyelectrolytes were compacted into unimolecular micelles in which pAA chains were stretched away from the polystyrenic core. It was determined by DLS studies that the brush polyelectrolytes in the solutions could coexist as unimolecular micelles (R_h 3-10 nm), compact assemblies (R_h 15-40 nm), and large aggregates (R_h 130-370 nm). R_h values of brushes were higher in DO, in contrast to DMF solutions, which promoted formation of more compact unimolecular micelles. The intermolecular hydrogen bonding was found to be dominant when 10-20% of water was present in the solutions. Higher temperature promotes intermolecular interaction and aggregation of brush polyelectrolytes. No substantial differences in aggregation behavior between random and diblock polyelectrolytes were observed. Water static contact angle (WCA) was used to examine wetting of the surfaces coated by bottle-brush polyelectrolytes. Solutions (0.5 w/v %) of polystyrenic copolymers in THF and brush PE in DMF were spin coated onto clean glass substrates. Contact angle measurements were done by sessile drop method. It was determined that WCA of the surfaces coated by bottle-brush polyelectrolytes films was significantly lower (~60-70º) compared those coated by corresponding polystyrenic backbones (~90-92º). In turn, the films of block-type brushes demonstrated higher WCA values (70-73º) in comparison with those of corresponding random brushes (55-69º). Rather high WCA values of bottle-brush polyelectrolytes films can be assigned to very hydrophobic backbone and terminal hydrophobic CTA moieties.

Acknowledgements. Financial support from the Research Council of Lithuania under the project MIP-54/2015 is gratefully acknowledged.

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PAN NANOFIBRES AS A MATRIX FOR CATALYST SYNTHESIS

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Electrospinning is a method to produce fibers by the use of electric force to draw charged threads of a polymer solution and reach the diameters in the range of several micrometres down to tens of nanometres. This property together with the big surface area and porosity make these nonwoven mats suitable candidates for solid supports of surface area-dependent functional materials such as sensors, catalysts [1]. Polyacrylonitrile (PAN) and its copolymers are the most common precursors for the production of carbon nanofibers as well as activated carbon nanofibers. The combination of the metal nanoparticles and specific surface area of polymer nanofibers gives the unique optical, electrical and catalytic properties of material. Therefore, the incorporation of TiO_2 nanoparticles into PAN fibers exhibits excellent catalytic activity [2]. The synthesis of TiO_2 nanocatalyst by electrospinning technique is presented in this paper.

PAN (with $M_w=1.5\cdot10^5$ g/mol), titanium isopropoxide (TTIP), acetic acid, DMF were used as received. PAN was dissolved in DMF under heating to form solution of 10 wt%. In a separate vial certain amount of DMF, glacial acid and TTIP was mixed. Then the latest solution was slowly dropped into the first one. The prepared solution was loaded into syringe equipped with 23G needle. The voltage source of 27 kV was used. The rotating collector was covered with stainless steel plate. The distance between the tip of needle and collector was fixed at 22 cm. The feed rate of the solution was kept in a range of 0.7–0.8 ml/h. As spun fibers were calcined at 450-750°C for 2 h in air, in order to eliminate the organic components and to activate the crystallization of titania. Images of morphology of the samples were obtained by SEM, the crystallinity was determined by XRD, BET theory was used to determine the surface area and porosity.

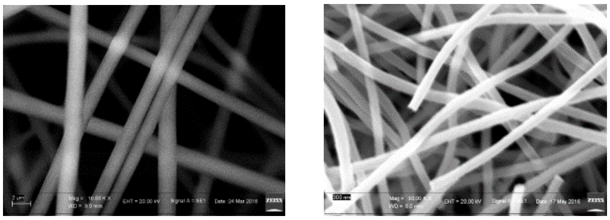

Fig. 1. SEM images of as spun (left) and calcinated fibres (right)

The fiber layer was characterized as smooth and uniformly deposited with diameters of fibers in range of 250-350 nm. It can be seen that the diameter of fibers reduced about 4 times after calcination (Fig. 1). The calcinated fibres were mainly composited of TiO_2, with additions of carbon as a product of the calcination of PAN. TiO_2 particles were uniformly distributed. Relatively high surface area and pore volume of 32 m^2/g and 110 mm^3/g were determined. Titanium alkoxides phase transformation occurs at a temperature higher than 600°C in this experiment.

TiO_2 nanofibers were successfully synthesized by electrospinning method using PAN/DMF/TTIP solution. Electrospun TiO_2 shown properties have great potential for applications as photo catalysts.

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IN-SITU PREPARATION OF POLYMERIC NANOCOMPOSITES ON THE BASE OF POLY(METH)ACRYLATES AND SURFACE MODIFIED DETONATION NANODIAMONDS

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Detonation nanodiamonds (DND) are of the great interest as a filler for preparation of polymeric nanocomposites. There are literature data of both the influence of DND on polymers physical properties and the absence of such dependence. It can be caused of difference in surface nature of DNDs used in the studies. Nowadays it is well known that DND surface contains tertiary alcohol groups and carboxylic ones as a result of technology of their production. It obviously leads to 1) poor surface wettability of non- and low-polar liquids including most of vinyl monomers; 2) high tendency of water adsorption and 3) high possibility to form bulky secondary structures caused by H-bonds. In the last case aggregates is formed of the size 2-3 order of magnitudes higher than individual DNDs, total surface of filler dramatically decreases and its influence on the composite properties should not be expected.

In this study surface functionalization was used to solve the problem. –OH and –C(O)OH groups on the surface were replaced by $–C(O)O–CH_2C_4F_9$ (**I**), $–C(O)O–Si(CH_3)_3$ (**II**) and $–O(CH_2)_2–Si(CH_3)(OSi(CH_3)_2)_2$ ("umbrella"). It was established that the average size of DND aggregates is 10^3-10^4 nm while the particle size distribution of surface functionalized DND has a maximum at about 10^2 nm. It made possible to obtain stable sols of DND in monomer. Under ultrasound their sols in acrylic and methacrylic monomers were obtained.

An interesting effect of surface functionalized DND on molecular mass characteristics of poly(methyl methacrylate) (MMA) synthesized was found. In the case of perfluoroalkyl functionalized (**I**) DND MM slightly decreases and polydispersity becomes more narrow. If the trimethylsilyl functionalized (**II**) DND was used MM increased but polydispersity index also decreased. In the table below molecular mass characteristics of poly(MMA) synthesized in the presence of "umbrella type" functionalized DND are shown. M_w and M_n slightly decrease with increasing of DND concentration; molecular mass distribution becomes wider. Polymerization was carried out in bulk, at 60-70°.

Table. Molecular mass characteristics of poly(MMA) obtained in the presence of different concentration of "umbrella type"surface modified DND

DNA concentration, mass.%	M_w	M_n	M_w/M_n
0	3 800 000	740 000	5.20
0.01	3 720 000	620 000	6.01
0.05	3 680 000	650 000	5.65
0.1	3 600 000	610 000	5.87

For some acrylic monomer traditional radical polymerization in bulk leads to obtaining cross-linked, non-soluble polymers. Their further processing is impossible. By the example of propylacrylate it was shown that using of addition-fragmentation chain transfer allows to avoid this trouble.

POROUS MODIFIED POLY(URETHANE-UREA) MICROPARTICLES AS A CARRIERS FOR MALTOGENASE IMMOBILIZATION

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An ideal matrix for enzyme immobilization should be biocompatible without compromising the protein structure and thereby it's biological activity [1]. In our previous study, maltogenase was immobilized onto polyurethane-urea (PUU) microparticles based on poly(vinyl alcohol) (PVA). Good mechanical properties of PUU microparticles and no volume change after storage in sodium citrate buffer were observed. Those properties provided potential for use of PUU microparticles as a carrier for immobilization of enzyme for industrial processes [2-4].

Herein, synthesis of PUU microparticles based on PVA and 4,4'-methylenebis(cyclohexyl isocyanate) (DCHDI) and application for immobilization of maltogenase (starch hydrolyzing enzyme) were presented.

Surface area, cross-linking density and porosity of obtained PUU microparticles were regulated by modification of PUU microparticles with various diamines, such as ethane diamine (EDA), butane diamine, propane diamine and melamine. Increasing in amount of diisocyanates in initial molar ratio resulted in increasing amount of urea segments in the PUU microparticles. Structure of microparticles was proven by FT-IR spectroscopy and analytical chemical methods. All FT-IR spectra of the PUU microparticles show the same band at 3334 cm^{-1} related to NH, bands at 2918 cm^{-1} and 2850 cm^{-1} relating to C-H from alkyl groups, band at 1634 cm^{-1} related to C=O of the urea group, band at 1547 cm^{-1} is assigned to amide II (δ N-H, ν C=N), band at 1226 cm^{-1} is assigned to amide III (another type of δ N-H, ν C=N) and band at 1027 cm^{-1} (ν C-O-C) is assigned to ether linkage and a small shoulder at 1691 cm^{-1} is related to C=O of the urethane group.

It was estimated, that surface area was increased from 7.3 to 37.4 m^2/g with increasing amount of diisocyanate in initial reaction mixture. Modification of PUU microparticles with various diamines also leads to increase surface area and total pore volume. The highest surface area (45.7 m^2/g) of PUU microparticles modified with EDA was achieved when initial molar ratio of PVA:DCHDI:EDA was 1:6:3. TGA curves of PVA-based PUU show three step decomposition profile. The first stage maximum decomposition temperature of PUU microparticles was around 260-268 °C. The second stage maximum decomposition temperature was in the range of 325-337 °C. The first two steps are decomposition of urethane and urea linkages, respectively. The third decomposition step at 410-418°C indicated decomposition of residue of the main PVA chain.

Biocatalytic activity of maltogenase bound to the PUU microparticles was investigated. During immobilization of maltogenase onto PUU microparticles, covalent binding was prevailed. Efficiency of immobilization of maltogenase onto this carrier was varied from 73.3 to 89.6 %. Immobilized MG was stable in time, after 50 days storage 82.3 % of residual activity was remained.

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STUDY OF MOLECULAR MASS CHARACTERISTICS OF POLY(N-VINYL SUCCINIMIDE) OBTAINED VIA RAFT POLYMERIZATION

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Nowadays controlled radical polymerization technics of addition-fragmentation chain transfer (RAFT) is the most promising method of synthesis of polymer with precisely defined molecular mass (MM) characteristics and complex macromolecular architecture, and also gives a unique opportunity to obtain polymers of narrow MM distribution under the conditions typical for conventional radical polymerization. It completely concerns to N-vinyl succinimide (VSI) polymerization in bulk. Obtaining soluble narrow-dispersed VSI homopolymer by traditional polymerization is impossible because of the chain transfer reaction to VSI cycle methylene protons leading to cross-linked product. This problem can be solved by using RAFT polymerization in the monomer melt (VSI melting point 48.5°C) for example in the presence of dibenzyl trithiocarbonate (BTC) as a RAFT agent and using common for radical polymerization initiator azobisisobutyronitrile (AIBN). The main MM characteristics of poly(VSI) samples studied are presented in the table below.

Table. Reaction conditions and molecular mass characteristics of poly(VSI) samples synthesized in the presence of BTC

		VM1	VM2	VM3	VM4
[AIBN], mol/l		10-3	0 (thermal initiation)	10-3	10-3
[BTC], mol/l		10^{-2}	10^{-2}	10^{-1}	$5\cdot10^{-2}$
Conversion, %		72	54	24	44
M_n(from NMR data), g/mol		67 800	50 300	4 500	–
MM calculated, g/mol		72 000	54 000	2 400	–
GPC data	M_n, g/mol	47 800	54 000	7 300	–
	M_w, g/mol	88 500	74 900	8 800	–
[η], dl/g		22.1±0.1	29.3±0.3	7.40±0.01	12.42±0.08
M_{sD}, g/mol		57 000	68 000	5 400	15 700

Due to the scheme of RAFT polymerization and in the case of effective RAFT agent (when polymer chains forming from the initiator radicals can be disregarded) M_n can be calculated by the equation:

$$M_n = M_{RAFT} + \frac{q\cdot[M]_0}{[RAFT]_0}\cdot M_M,$$

where M_{RAFT} – RAFT agent molecular mass, q – monomer conversion, $[M]_0$ and $[RAFT]_0$ – the initial concentrations of monomer and RAFT agent, M_M – monomer molecular mass. The results are shown in the table.

The absolute molar masses were estimated from the data of sedimentation-diffusion analysis (sedimentation coefficient *s* and translational diffusion coefficient *D*). Velocity sedimentation was investigated using a Beckman XLI analytical ultracentrifuge and translational diffusion was studied on a Tsvetkov polarizing diffusometer. Viscosity measurements were carried out using an Ostwald viscometer.

SYNTHESIS AND PROPERTIES OF METHYLMETHACRYLOYL MONOMER CONTAINING NAPHTHALIMIDE AND TRIPHENYLAMINO MOIETIES

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The main difficulty in the preparation of organic light emitting diodes and other optoelectronic devices by solution processing is the solubility of the material which forms the bottom layer onto which the top layer has to be cast, because most organic semiconductors are soluble in the same solvents. One approach that was employed to circumvent this problem is the appliance of electro-active derivatives with reactive functional groups, which could be converted into polymers with lower solubility or even into insoluble networks by cross-linking reactions [1]. High electron-affinity of naphthalimides determines the possibility of their use as electron-transporting media, and the imide nitrogen makes naphthalimides easy to functionalize [2]. They exhibit good photochemical stability and high luminescence quantum yields [3].

In this work we report on the synthesis and investigation of methylmethacryloyl monomer containing naphthalimide and triphenylamino moieties which was synthesized by condensation and palladium-catalyzed Suzuki-Miyaura reactions (Fig.1).

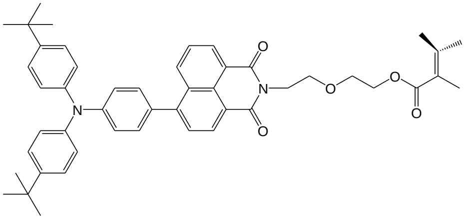

Figure 1. Structure of naphthalimide-based monomer.

The structure of the synthesized compound was proved by ^{1}H and ^{13}C NMR, IR and mass spectrometries. The thermal, optical, electrochemical and photophysical properties of the synthesized compound were investigated. The synthesized molecule exhibit moderate thermal stability with the thermal degradation onset temperature at 215 ^{o}C. Absorption peak which appear at 433 nm apparently corresponds to the intramolecular charge-transfer transition between the triphenylamino donor moiety and the naphthalimide acceptor moiety. The estimated optical band gap of the monomer was 2.49 eV. The dilute THF solutions (10^{-5} M) of the monomer showed orange luminescence peaking at 647 nm after excitation with the wavelength of 450 nm. The ionization potential and electron affinity values of the monomer were estimated by cyclic voltammetry and were found to be 5.51 and -3.72 eV, respectively.

Acknowledgements
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SYNTHESIS OF COPOLYMERS OF N-VINYL SUCCINIMIDE WITH VINYL ACETATE FOR IMMOBILIZATION OF LOW MOLECULAR SUBSTANCES

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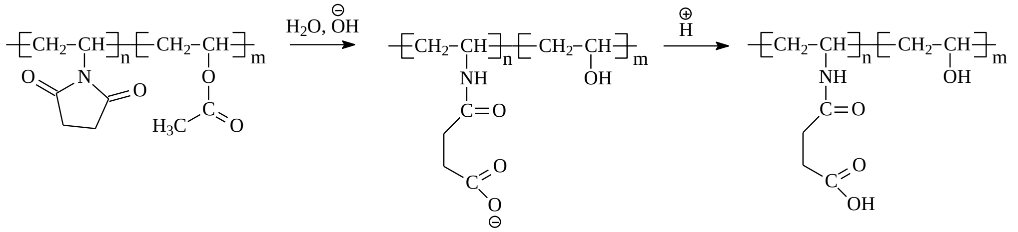
Copolymers of N-vinylsuccinimide (VSI) and vinyl acetate (VA) are of great interest as precursors for the preparation of water-soluble polymeric matrix capable of immobilizing the low molecular weight substances including medicines. The advantage of these polymers like copolymers of vinyl amino succinic acid and vinyl alcohol is their non-toxicity. They can be easy synthesized from poly(VSI-VA) by alkaline hydrolysis followed by conversion of the carboxyl groups in the salt form to acid one using any suitable ion exchange resin:



Many drugs are organic bases and can be easily immobilized on such matrix due to the formation of ionic bonds. Application of the polymer complexes as new medicinal forms and as a part of more complex therapeutic systems imposes high requirements to the matrices including molecular mass and compositional homogeneity of the copolymers. It is extremely difficult to satisfy them if you limit yourself of classical radical polymerization.

In this study the results are presented achieved in the synthesis of poly(VSI-VA) with predetermined molecular mass characteristics and high compositional homogeneity using the most modern techniques of controlled radical polymerization – RAFT (reversible addition-fragmentation chain transfer) polymerization. Dibenzyl trithiocarbonate (BTC) was chosen as a RAFT agent as the most available and versatile for a wide range of vinyl monomers. In addition to these advantages under the RAFT polymerization it is possible to carry out the polymerization in bulk of the monomers without using of toxic organic solvents, and at the same time without the risk of obtaining of cross-linked insoluble products which is common for the classical polymerization.

The samples of poly(VSI-VA) trithiocarbonates were obtained at three initial compositions of the monomers mixture, covering the entire practically interesting range: 25-75 mol. % of VSI. It is shown that in all cases molecular mass growths with conversion, which is a main feature of controlled radical polymerization. This indicates sufficient efficiency of BTC in copolymerization of VSI with BA, despite the fact that in the corresponding homopolymerization it is effective only for VSI. This confirms our earlier assumption that a satisfactory control in the RAFT polymerization can be achieved under the condition of high efficiency of RAFT agent only to the more active monomer in the monomers pair.

SPECTROSCOPICAL INVESTIGATION OF VARIOUSLY OPENED UP DERMA

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The leather industry is one of the most environmentally polluting branches of industry, especially due to its waste waters. Huge amounts of lime sludge and total solids formation are the main drawbacks of lime.[1] Herewith, the cleaning of unhairing solutions, polluted with lime, sulphides and the products of protein degradation, remains very difficult and expensive.

Sodium aluminate can be used instead of lime for lime-free unhairing of hides.[2] The qualitative removal of hair is achieved using a solution containing 2–3% of sodium aluminate and 1.3–1.5% of sodium sulphide. The effect of such a process on collagen is weaker than that of the conventional one. Increase of the temperature up to 30°C does not lead to better hair removal but significantly enhances the effect on collagen.

Effect of the unhairing-derma opening up method on collagen as the main protein of hide was tested using infrared spectroscopy analysis. The spectrum of unhaired-derma opened up hide using calcium hydroxide as conventional agent was recorded as well. Software ”Spectrum 5.0.1“ was used calculating the area of peaks in spectrums ΔS ($A \cdot cm^{-1}$).

The comparison of infrared spectrums of the variously treated hide has shown that in all spectrums are identic peaks and this lets conclusion that any serious changes in supermolecular structure of collagen do not occur during unhairing-derma opening up process.

Assessment of peaks intensities allows proposition that derma opening up method using NaOH should be provided for the derma opening up process of the hide unhaired with sodium aluminate. The effect on collagen during unhairing using only the sodium aluminate is less than that of conventional liming. This conclusion approved the conclusion made after estimation of physical and chemical properties of hide after unhairing-derma: the addition of 0.5% NaOH allows better opening up of the derma to be obtained.

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EFFECT OF $iBuAlCl_2$ PRE-ACTIVATION ON THE ISOBUTYLENE POLYMERIZATION IN NONPOLAR SOLVENT IN THE PRESENCE OF ETHERS

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Polyisobutylene (PIB) with high *exo*-olefin end groups content and low molecular weight (M_n ~ 500–5000 g/mol), also called highly reactive PIB (HR PIB), is a key intermediate in the preparation ashless additives for motor oil and fuel. In recent time, several new methods based on using alkylaluminium dichlorides in the presence of different ethers have been reported for the synthesis of HR PIB in nonpolar solvent [1-3]. However, the main disadvantage of these methods is low monomer conversion (≤30 %).

In this work, the cationic polymerization of isobutylene using $iBuAlCl_2$ pre-activated by the wet argon, $MgSO_4{\times}7H_2O$ and pure water in the presence of diisopropyl ether or mixture of two ethers in *n*-hexane at 10°C and high monomer concentration ([IB] = 5.8 M) has been investigated (Table 1). We showed that highest yield of HR PIB reaches using method **II**, but MWD in this case is rather broad. It was established that method **III** afforded PIB*s* with lower polydispersity, while at reduced i-$Pr_2O/iBuAlCl_2$ molar ratio monomer conversion increases, without any effect on *exo*-olefin end groups content. We found also that equimolar mixture of i-Pr_2O with Et_2O allows to increase the monomer conversion; moreover, this approach afforded HR PIB*s* with narrower MWD in comparison with that obtained with neat i-Pr_2O. It should be noted that required low molecular weight (M_n(SEC) ≤ 1500 g/mol) was obtained in all cases (Table 1).

Table 1. Influence mode of pre-activation of $iBuAlCl_2$ on cationic polymerization of isobutylene in the presence of ethers in *n*-hexane at 10 °C[a]

Mode of pre-activation	Ether	R_2O/ $iBuAlCl_2$, mol/mol	conv,%	M_n(SEC), g/mol	M_w/M_n	*Exo*-olefin end groups,%
-	i-Pr_2O	0.8	46	1300	3.8	90
I	i-Pr_2O	0.8	73	1485	2.9	83
II	i-Pr_2O	0.8	82	1390	3.9	78
III[a]	i-Pr_2O	0.8	62	1070	2.8	81
III[c]	i-Pr_2O	0.8	68	1120	3.4	80
III[c]	i-Pr_2O	0.4	94	1210	3.7	80
III[c,d]	Et_2O/i-Pr_2O	0.4	80	1230	2.6	83
III[b,c,d]	Et_2O/i-Pr_2O	0.4	91	1150	2.7	82

[a][$iBuAlCl_2$] = 22 mM; [H_2O] = 0.033 M; [IB] = 5.8 M. Reaction time: 10 min. H_2O introduced after 3 min since introduction of isobutylene. **I** – pre-activation by pure water; **II** – catalyst was pre-activated by bubbling of wet argon through the solution of $iBuAlCl_2$ in *n*-hexane during 10 min; **III** – catalyst pre-activation by $MgSO_4{\times}7H_2O$ (15 mol% of H_2O to $iBuAlCl_2$). [a]H_2O introduced before $iBuAlCl_2$. [b]Reaction time: 15 min. [c][$iBuAlCl_2$] = 38 mM; [d] Et_2O/i-Pr_2O = 1.

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IONIZATION ENERGY STUDIES OF P3HT-PCBM INTERFACE USING PHOTOEMISSION YIELD SPECTROSCPOY

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The efficiency of organic photovoltaic cells is determined by energy level compatibility at the electrode/organic compound interface as the charge carrier extraction from the active layer is one of the main parameters that affect the performance of solar cell. When decreasing film thickness, ionization energy and electron affinity level value shift can be observed due to the Fermi level alignment between two different materials. In that case energy level values that are obtained from bulky layers cannot be used anymore. Until now energy level shift at the metal/organic interface is being actively studied. Electron transfer from electron donor to acceptor molecule has the same importance. This is why information about energy level values of organic materials at the organic-organic interface is critical.

Ionization energy shift at organic-organic interface was studied using photoemission yield spectroscopy. In this work interface between two well-known organic photovoltaic materials- polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) and fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) was studied.

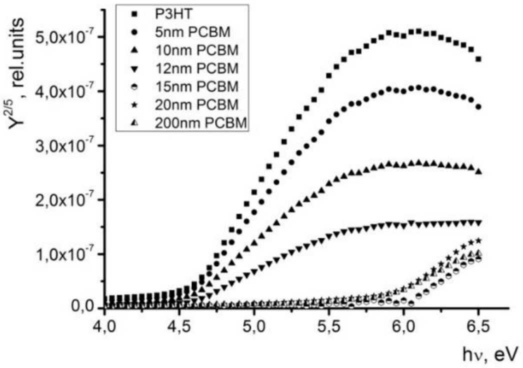

Fig. 1. Photoemission yield spectra of planar heterojunction P3HT/PCBM samples depending on PCBM layer thickness

Two kinds of samples were made- planar heterojunction samples and bulk heterojunction samples. In the first case PCBM was thermally evaporated on top of the spin-coated P3HT layer creating planar heterojunction. Ionization energy of P3HT and PCBM dependence on PCBM layer thickness was studied. In the other case the bulk heterojunction samples were made by spin-coating. Here mass ratio of P3HT:PCBM in the solution was varied. Two series of bulk heterojunction samples were made by varying solvent: chloroform or chlorobenzene was used.

Sample morphology was studied by scanning electron microscope.

Relation between ionization energy of organic compounds and sample structure will be discussed.

Acknowledgements

Financial support provided by Scientific Research Project for Students and Young Researchers Nr. SJZ2015/20 realized at the Institute of Solid State Physics, University of Latvia is greatly acknowledged.

ANIONIC RING-OPENING POLYMERIZATION OF CARBAZOLE-CONTAINING THIIRANE MONOMERS

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Carbazole-based polymers are promising materials as hosts in polymer light emitting devices [1]. Cationic [1] and photoinitiated cationic [2] polymerization of 9-(thiiran-2-ylmethyl)-9H-carbazole (TPK) resulted in low molecular weight polymers (M_n up to 3100 g mol^{-1}) with high polydispersity (M_w/M_n=4-8). Thiolate ions are well-known initiators in thiirane polymerization, but under investigated conditions anionic ring-opening polymerization (AROP) was not controlled [3]. Living AROP of methylthiirane took place in hexanethiol/1,8-diazabicyclo[5.4.0]undec-7-ene initiating system, giving polymers with high M_n (up to 12000 g mol^{-1}) and low polydispersity (M_w/M_n=1.12) [4].

Here, we report the AROP of thiirane derivatives TPK and 3,6-di-*tert*-butyl-9-(thiiran-2-ylmethyl)-9H-carbazole (TKK) initiated by hexanethiol/1,5,7-triazabicyclo[4.4.0]dec-5-ene system in THF at [Monomer]/[Initiator] = 20 for the first time.

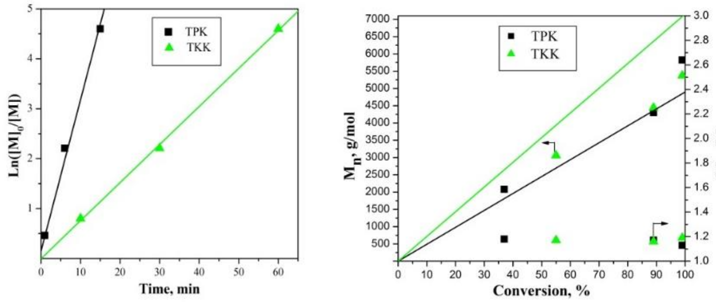

Fig. 1. First-order plots and M_n, M_w/M_n vs. conversion plots for TPK and TKK polymerization

Polymerization of both monomers proceeds smoothly to afford complete monomer conversion in 15 min and 60 min for TPK and TKK, respectively (Fig. 1). The first-order plots were linear for both monomers. The M_n*s* of the obtained polymers increased in direct proportion to monomer conversion for TPK and TKK, while a good correlation between experimental values of M_n and calculated ones for TPK was observed. In addition, all polymers were characterized by narrow molecular weight distribution (M_w/M_n=1.2).

Acknowledgements

This work was supported by the Belarusian Republican Foundation for Fundamental Research (grant No. X15ЛИТ-010) and Research Council of Lithuania (grant No. TAP LB-03/2015).

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ELECTROCHEMICAL CHARACTERIZATION OF SMALL MOLECULE BASED OLED'S AND THEIR ACTIVE COMPOUNDS

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A number of p-phenylene based commercial organic that were previously shown to act as a promising components of high-efficient organic light emitting diodes (OLEDs) were investigated by cyclic voltammetry and electrochemical impedance spectroscopy.

Electrochemical impedance spectra of Pt electrode in CH_2Cl_2 solutions containing investigated compound and Bu_4NBF_4 as electrolyte were obtained and analyzed by deriving electrochemical electrical circuit and determination of its parameters. Charge transfer resistance, double layer capacitance and other parameters were calculated and represented as a function of potential. Combined analysis of charge transfer resistance and diffusion impedance values allowed estimation of rate constant for compound oxidation and reduction processes in solution on Pt electrode.

The characteristic values of the compounds are expected to be close to their charge transfer parameters in solid state devices. The latter are the object of further investigation.A brief paragraph with Acknowledgements may be added at the end of the main text.

A number of devices composed of TPB, TCBPA, TAZ and TPBi layers and ITO and Al/LiF (as border conductive layers) were investigated by electrochemical impedance spectroscopy.

Electrochemical impedance spectra of the devices were analyzed by equivalent electric circuit method. The capacitance and resistance values of each layer were obtained and analyzed separately. Due to separate analysis of layers the mechanism of charge transfer was proposed. Charge carrier mobilities in the hole-transport and electron-transport layer were estimated from layer conductivities as functions of applied voltage.

PHOTO-CURABLE GLYCEROL-BASED POLYMERS WITH STRUCTURALLY DIFFERENT ALCOHOLS

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Photopolymerization technology is rapidly growing due to its advantages, i.e. insensitivity to oxygen, low polymerization shrinkage, and economical benefit [1, 2]. The polymeric systems cured by radiation have numerous applications in the different industries such as coatings, paints, printing inks, and adhesives [3]. Glycerol, the by-product of biodiesel refining is a promising candidate which can be used as monomer in the synthesis of polymers as it is or after chemical modification [4]. Coatings obtained from epoxy resins are often wrinkled, therefore to avoid this disadvantage alcohols can be used as modifiers of coating systems [5].

The cross-linked polymers were obtained by photopolymerization of glycerol diglycidyl ether with structurally different alcohols, i.e. 1,4-cyclohexanedimethanol, 1,1,1-tris(hydroxymethyl)propane, hydroquinone, and bisphenol A. The mixture of triarylsulfonium hexafluoroantimonates was used as photoinitiator. The 10, 20, and 30 mol. % concentration of the alcohols was used in the batches. The chemical structure of the photocross-linked products was confirmed by IR spectroscopy. The yield of the insoluble fraction of the cross-linked polymers obtained after Soxhlet extraction in chloroform for 72 h was in the range of (85-99) %. Thermogravimetric analysis showed that the synthesized polymers were thermally stable up to 300 ^{o}C. The differential scanning calorimetry measurements revealed that all the photocross-linked polymers were the amorphous materials with the glass transition temperatures in the range of (6-22) ºC. The swelling values of the photocross-linked polymers ranged from 6.9 % to 8 %. The Young modulus values of the polymer films were in the range of (126.80-468.40) MPa. The elongation at break values were in the range of (9.19–78.60) %. The tensile strength values ranged from 6.79 MPa to 22.73 MPa. The cross-linked polymers were found to be biodegradable in natural environment. The obtained results demonstrated that the mechanical, thermal properties, swelling in water, and biodegradability of the glycerol-based polymers could be controled by modifying with structurally different alcohols.

Acknowledgements

Financial support from the Research Council of Lithuania (project No. MIP-066/2015) is gratefully acknowledged.

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POLYMERIC COMPOSITES FOR RECONSTRUCTION OF HOOVES

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Foot health and lameness are major issues facing dairy producers because of their common occurrence and the tremendous economic losses incurred. Early detection and prompt treatment can minimize the loss, improve recovery, and reduce animal suffering. Over the last 20 years, significant advancements in composite adhesive technology have made hoof repair/reconstruction easier, more cost- effective, and much more functional [1]. The hoof treatments can consist of hoof trimming, foot baths, and acrylic hoof repair [2]. The crack is drilled out and cleaned, and acrylic material is placed in it [3]. This holds the crack together and prevents further spread of the crack; the hoof grows out on the crack heals. Acrylic hoof repair systems are primarily composed of polymethyl methacrylate (PMMA) [1]. PMMA-based acrylic hoof repair/adhesive systems are generally two-component systems that are mixed by hand containing various amounts of the composite. These systems cure (set up) in 2 to 15 minutes depending on the compound, humidity, and ambient temperature.

The aim of this work was to evaluate the effect of methyl methacrylate (MMA) and hydroxyapatite (HA) amount on the mechanical properties of polystyrene-*block*-polybutadiene-*block*-polystyrene based hoof repair systems. To this end, various compositions of polystyrene-*block*-polybutadiene-*block*-polystyrene based hoof repair systems which differed in amount of methyl methacrylate (MMA) and hydroxyapatite (HA) were prepared. During the polymerization the maximum temperature at the surface varied from 31.8 °C to 53.0 °C. The handling time varied from 5.16 min to 12.00 min. The mechanical properties of prepared samples were compared with natural hoof of dairy cattle mechanical properties.

Acknowledgements

Financial support from the R&D and Innovation Fund of Kaunas University of Technology (grant No. MTEPI-L-16006) is gratefully acknowledged.

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SYNTHESIS AND STUDY OF DICYANOBENZENE-BASED MATERIALS

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The design and characterization of materials exhibiting thermally activated delayed fluorescence (TADF) for optoelectronic applications represents an active area of recent research [1-3]. Noble metal-free TADF molecules offer unique optical and electronic properties arising from the efficient transition from the lowest triplet (T_1) excited state to the first excited singlet (S_1). Their ability to harvest triplet excitons for fluorescence through facilitated reverse intersystem crossing ($T_1 \rightarrow S_1$) can directly impact their properties and performances, which is attractive for low-cost efficient organic light emitting diodes. To develop high-efficiency TADF materials, it is necessary to design molecules with excellent EL characteristics while maintaining a small ΔE_{ST}. A small ΔE_{ST} can be obtained by introducing electron-donating and electron-accepting groups into molecules to decrease the spatial overlap between HOMO and LUMO orbitals.

We designed and synthesized new molecules, in which the acceptor dicyanobenzene unit is used as the central skeleton and donor acridine, phenothiazine or dimethoxycarbazole moieties are appended to the skeleton (Fig. 1). Comparative study on the thermal, optical and photoelectrical properties of the compounds will be presented.

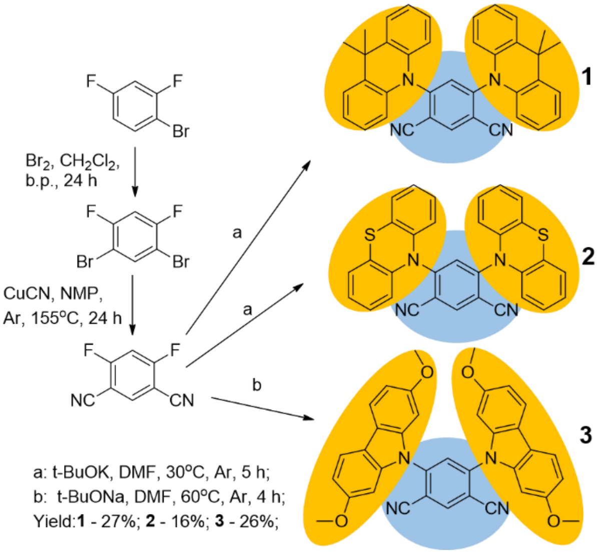

Fig. 1: Structures of benzonitrile-based derivatives

Acknowledgements
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INVESTIGATION OF EXCIPLEX EMITTERS FOR OLED APPLICATION

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Investigation of the kinetics and mechanism of electrochemical processes in organic compounds is important for the designing of new emitters and OLED devices. One of the selected methods of analysis was cyclic voltammetry (CV), which allows to investigate the quasireversible processes in the system.

Samples, which were chosen, have different structures and properties. From CV it was determined basic characteristic, sush as oxidation and reduction potential, was calculated HOMO/LUMO energy levels, predicting pairs, which are able to form exciplex complex, and therefore can be a component of the active layer.

Fluorescence investigation was done for samples and there are some changes in some spectra of mixture of components compared to the pure components. It can be the formation of new bonds or to obtain a stable complex.

SYNTHESIS OF WELL-DEFFINED BRUSH POLYMER BLOCKS VIA RAFT TECHNIQUE

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Over the past few years, the well-defined brush-type copolymers containing poly(ethylene oxide) (PEO) side chains showed growing scientific impact and already became versatile materials in bio-[1] and nanotechnology[2,3]. Due to their unique properties such as solubility in most solvents, biocompatibility, and non-toxicity, they are applied as nanocarriers for drug delivery systems, biofouling resistants[1], surface modifiers, lubricants, super-dispersants[3], flocculants and rheology modifiers[2].

The successful synthesis of four different poly(ethylene oxide) methacrylate (PEO_xMEMA) polymers differing in length of PEO side chains (x = 5, 9, 22, 45) were carried out at different reaction conditions. The effect of RAFT agent and thermal initiator ratio on reaction control as well the kinetic aspects of polymerization was fully investigated during these studies. The all synthesized p(PEO_xMEMA) exhibited narrow molecular weight distribution ($M_w/M_n < 1.2$) and the determined values of absolute molecular weight showed perfect correlation to theoretical. The different block polymers with well-defined structure and predetermined molecular weight were synthesized by chain extension reaction using first block as RAFT agent for controlled polymerization (Fig. 1.). The chain extension reaction of different PEO_xMEMAs and cationic METAC exhibited acceptable control with use of low side chains containing $pPEO_xMEMA$ RAFT agents (x = 5, 9) however, the used of relative long side chain containing RAFT agents (x = 22, 45) resulted of higher dispersity products (M_w/M_n up to 2) and the MWD exhibited multimodal distribution.

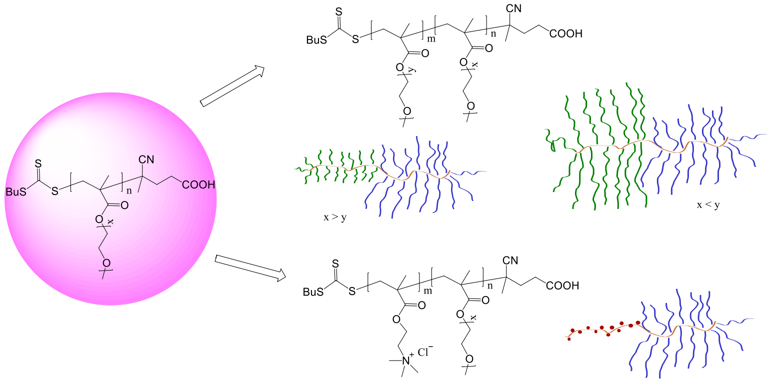

Fig. 1. Schematic illustration of brush block building via RAFT method

Acknowledgements

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COMBINATION OF AGGREGATION-ENHANCED EMISSION AND THERMALLY ACTIVATED DELAYED FLUORESCENCE OBSERVED IN THE DERIVATIVES CONTAINING DONOR AND ACCEPTOR MOIETIES

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Employment of emitters exhibiting thermally activated delayed fluorescence (TADF) for the fabrication of organic light emitting diodes (OLEDs) allows to abandon the high-cost phosphorescent materials based on rare earth metals [1]. TADF is observed in organic molecules with low differences between the first singlet (S1) and the first triplet (T1) energy levels due to the reverse intersystem crossing (RISC) from T1 to S1 and radiative decay from S1 to the ground state (S0)[2]. To achieve small difference between S1 and T1 (ΔE_{ST}), HOMO and LUMO orbitals of organic molecules have to be maximally separated which leads to the decrease of photoluminescence quantum yield(PLQY)of such molecules [1]. On the other hand, high PLQY of the solid-state organic materials can be achieved due to aggregation-enhanced emission (AEE) [3]. Therefore, the combination of both the TADF and AEE phenomena in organic emittersis of great interestfor the researchers engaged in the design and fabrication of highly efficient OLEDs.

In this work we report on the investigation of a series of derivatives by photoluminescence (PL) spectrometry. In the studied compounds which emit light in a blue-yellow region with fluorescence maxima in the range from 475 to 560 nm, both AEE and TADF were observed.

PL quantum yields of vacuum deposited layers were found to be higher than those of toluene solutions (~10^{-5}M) for all the studied compounds. For example, the highest PL quantum yield of the vacuum deposited layer of one compound at the ambient conditions was 51.7 % while that of dilute toluene solution was 7.2 %. This observation can be explained by the AEE effect. PL life times of the degassed toluene solutions of the compounds were up to the μs range while those of the non-degassed toluene solutions were in the ns range. In addition, the intensities of PL for degassed toluene solutions of the materials were up to 7.3 times higher than those for non-degassed toluene solutions. The phosphorescence and PL spectra of THF solutions at 77K were recorded to get singlet and triplet energy levels from the first maximum of PL and phosphorescence spectra, respectively. The triplet energy levels for the studied materials ranged from 2.55 to 2.87eV and were very close to their singlet energy levels showing singlet-triplet energy splitting smaller than 0.1eV which is sufficient for RISC. Therefore, long-life emission can be attributed to the TADF effect.

Acknowledgement: This work was supported by the Horizon 2020 ICT29-2014 project PHEBE (grant No. 641725).

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RAMAN SPECTROSCOPY OF THIN FILMS COPPER

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Thin metal films are objects with a very wide range of physical properties that significantly extends their practical application. Thin copper films on glass substrates were obtained using the vacuum deposition method during the current research. Thin films absorption and electrical resistivity (in the range from 5 Ohm to 10 MOhm) were controlled in different deposition conditions. It was theoretically shown in work [1] that in metal thin films, surrounded by dielectric, can occur plasmons with mean free path substantially exceeding the mean free path of plasmons existing at the metal-dielectric border. The properties of the surface plasmons essentially depend on thin films cluster structure with such significant parameter as ratio of cluster size to the size of gap between the clusters. The fig. 1, shows the Raman spectrum of copper films with an electrical resistance 7, 8, 10 Ohm, obtained in different conditions of vacuum deposition P7>P8>P10. It shows that film with the highest intensity of Raman scattering has an electrical resistance of 8 Ohm. This allows to conclude that there are the largest local fields in this film, determined by localized surface plasmons. Such films are of greatest interest. The measurements of absorption spectra in the visible range show that there is an absorption peak at 570 nm, which indicates the existence of copper oxide in the obtained films. This is confirmed by the electrical resistance of copper films increase occurred after air is admitted into evaporation chamber, and also by the Raman peak in the range of 560 cm^{-1}. Copper oxides are characterized by charge states capability, which is essential for plasmonic properties of thin films.

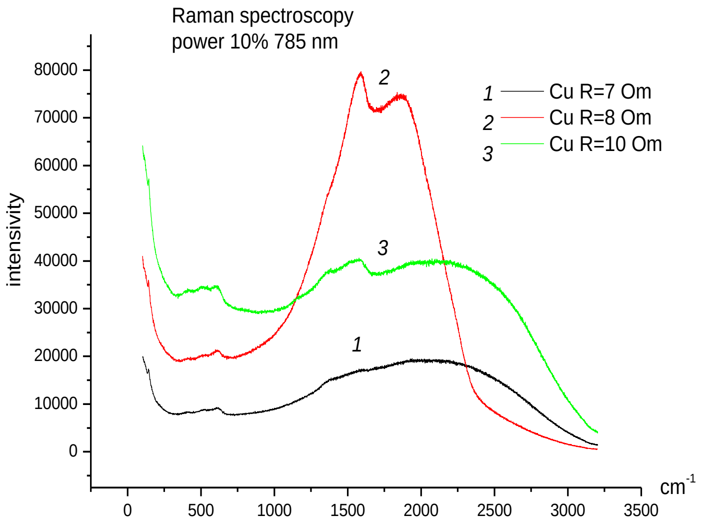

Fig. 1. Raman spectrum of copper films with an electrical resistance 7, 8, 10 Ohm

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NEW 3,6,9-TRIARYLCARBAZOLE-BASED MATERIALS FOR ORGANIC LIGHT EMITTING DIODES

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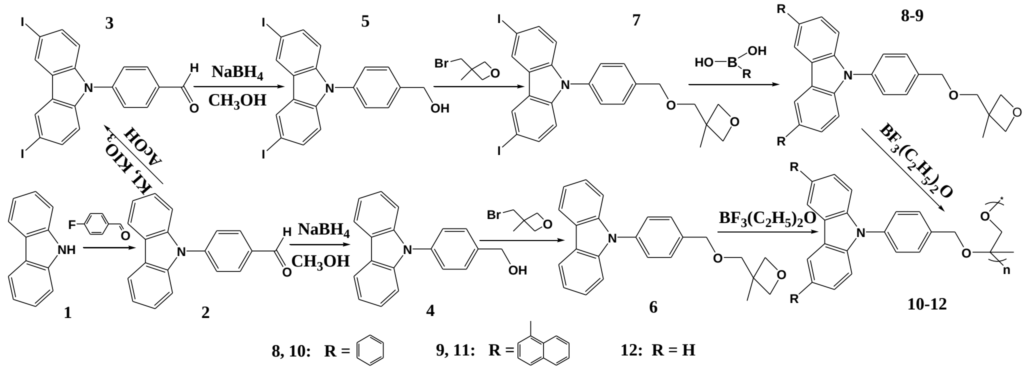
Organic light- emitting diodes (OLEDs) based on organic electro-active materials have attracted much attention because of their potential use in lighting as well as in flat panel displays [1,2], however efficient devices can be obtained only by building multilayer structures [3]. One method that is widely used to improve efficiency of the devices is the appliance of effective hole transporting layers in the structures of the OLED devices. The electroactive layers can be fabricated by vapour deposition or by spin coating from solution. The latter rout has some advantages, e.g. the production costs are reduced, large areas can be coated, and the molar mass of the materials is not limited. Here, we report on polymeric hole transporting materials containing 3,6,9-triarylcarbazole-based chromophores as electro-active moieties. The polymeric materials were fully amorphous with high glass transition temperatures. Hole transporting layers of the polymers were tested in OLEDs with Alq_3 emitter.

The synthetic rout demonstrating the preparation of polyethers (**10- 12**) containing electroactive chromophores is shown in Scheme. In the first step 4-(9-carbazolyl)benzaldehyde **(2)** was prepared from 9H-carbazole **(1)** by Tucker procedure. The aldehyde **2** was used for preparation of (3,6-diiodocarbazol-9-yl)benzaldehyde **(2)** using Tucker iodination method. Both the aldehydes **2** and **3** were then converted to hydoxy group containing compounds **4** and **5**, which were used for preparation of oxetanes **6** and **7**. Monomers **8** and **9** were obtained by Suzuki reactions of iodo-compound **7** with an excesses of phenyl boronic acid or 1-naphtyl boronic acid. All the oxetane-based monomers were polymerized by cationic polymerization in solution to afford polymeric materials **10-12**.



The electroactive polymers were tested as hole transporting layers in bilayer OLEDs of the structure ITO/**10, 11** or **12**/ Alq_3/LiF/Al. The devices with the polymer **11** containing electro-active di(1-naphtyl)carbazole units exhibited the best overall performance with turn on voltage of 4.4 V, maximum brightness of about 7500 cd/m^2 and current efficiency of 3.1 cd. These OLED properties are rather promising among electroluminescent Alq3-based two-layer devices.

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TERMOSENSITIVE GLYCOPOLYMER BOTTLE-BRUSHES

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Synthesis of glycopolymers has been widely reported in the last two decades [1,]. Glycopolymers are used as macromolecular drugs, drug delivery systems, cell culture substrates, stationary phase in separation systems and bioassays, responsive and catalytic hydrogels, surface modifiers, artificial tissues, and artificial organs substrates. Fortunately, advances in controlled radical polymerization allow precise control over polymeric structures and molecular weight making the synthesis of well-defined glycopolymers possible.

In this study we report the synthesis of sugar-based polymers of controlled structure prepared by reductive amination without protection of functional groups. First, two series of random and diblock copolymers containing the units of 2-dimethylaminoethyl methacrylate (DMAEMA) and 2-aminoethyl methacrylate hidrochloride (AEMCl) were synthesized by RAFT polymerization in 85-97 % yield and low dispersities (1.2-1.5). RAFT polymerization was carried out at 70°C in acetate buffer, pH 5.00. AEMCl content in the copolymers determined by ^{1}H BMR spectroscopy was from 30 to 70 mol%. Conversion of the monomers was monitored by ^{1}H NMR spectroscopy; molecular weight of the copolymers was determined by size-exclusion chromatography (SEC) with triple detection.Glycopolymer bottle-brushes were prepared in four steps starting from the synthesis of random copolymers of 2-hydroxyethyl methacrylate (HEMA) and DMAEMA. In the next step, hydroxyl groups of HEMA units in this polymeric backbone were esterified with 4-cyano-4-(butylsulphanylthiocarbonyl) sulphanyl pentanoic acid resulting in macromolecular multifunctional RAFT chain transfer agent (multiCTA). In the third step, RAFT copolymerization of AEMCl and DMAEMA from multiCTA generated molecular brushes containing primary and tertiary amino groups. And finally, glycopolymer linear and bottle-brushes were prepared by attachment of mannose, fructose, lactose, *N*-acetylglucosamine and dextran (M_n 4000 kg/mol) to the termosensitive DMAEMA “platforms” via reductive amination.

Chemical composition of the glycocopolymers containing mono-, di- and oligosaccharides was determined by ^{1}H NMR measurements. The signals at 0.86, 1.08, 1.94, and 4.18 ppm in ^{1}H NMR spectra of the glycocopolymers were assigned to the protons of polymethacrylate backbone, and the signals at 3.58-3.78 were assigned to the protons from 2-carbon to 6-carbon of the mono- and oligosaccharides. ^{1}H NMR spectra confirmed complete disappearance of a duplet of protons of anomeric carbon of the sugars at 5.09 or 4,82 ppm providing that glycosidic moieties have been coupled with the copolymers.

Solution properties of glycopolymers were examined by dynamic light scattering (DLS) and UV-VIS spectroscopy. It was shown that solutions of glycopolymers possessed lower critical solution temperature which decreased with increasing DMAEMA content in the copolymers.

Acknowledgements
Financial support from the Research Council of Lithuania under the project MIP-54/2015 is gratefully acknowledged.

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ONE-STEP SYNTHESIS OF DONOR-ACCEPTOR DERIVATIVES OF PENTACHLOROPYRIDINE, THEIR MODIFICATION AND PHOTOPHYSICAL PROPERTIES

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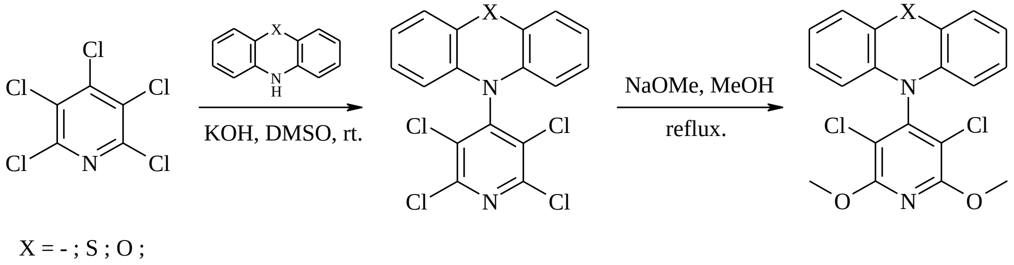
During the last two decades, organic light-emitting diodes (OLEDs) attracted great amount of attention as the devices for high-resolution and large area flat display panels. Extensive efforts have been made to improve electroluminescence efficiency[1] of OLEDs and a lot of studies have been focused on the enhancement of quantum efficiency of phosphorescent OLEDs with the appropriate host and phosphorescent materials. OLEDs based on thermally activated delayed fluorescence (TADF) represent the next generation of electroluminescent system and may provide a solution for the ultimate electroluminescence efficiency. Therefore, it has attracted much interest as alternative for fluorescence and phosphorescence based OLEDs due to an effective use of not only singlet excitons but also triplet excitons for fluorescence. TADF is possible because of reverse intersystem crossing from the triplet excited state (T_1) to the singlet excited state (S_1) [2]. In order to show TADF phenomenon, the materials should have a small energy gap between the excited singlet and triplet states ($\Delta E_{S\text{-}T}$).



The aim of our work was to find inexpensive and convenient synthetic pathway to obtain low-molar-mass donor-acceptor molecules with small energy gap between the excited singlet and triplet states. Carbazole, phenothiazine and phenoxazine were selected as donor moieties and pentachloropyridine was used as electron acceptor. After the synthesis of donor-substituted tetrachloropyridines we tried to modify photophysical properties by the attachment of methoxy groups to pyridine core. Methoxylation of pyridine core resulted in the significant shift of the wavelength of emission of compounds towards the blue region.

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STUDY OF THE PROPERTIES OF POLYOLEFIN BLENDS WITH DIFFERENT FILLER LOADING CAPACITY

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An effective way to improve the service properties of polymers is their modification with different fillers. The combination of polymers with fillers makes it possible to obtain materials with completely new service properties: loading polymeric materials with fillers improves their mechanical strength and hardness, reduces costs, and imparts special properties [1]. Fillers are loaded in order to modify polymers' adhesion capability, their frictional properties, electrophysical characteristics, thermal conductivity, etc. For example, for fireproofing the following mineral fillers as fire retarders are loaded into polymeric materials: clay, carbon nanotubes, hydroxides of magnesium, aluminum, oxides of silicon, titanium and others [2-3]. The influence of particulate filler on the mechanical and other properties of polymeric materials largely depends on its properties. In case filler concentrations exceed the optimum, polymeric material's strength loss is possible. Therefore, with the aim of composing tailor-made polymer composite materials it is necessary to know not only the fillers' characteristics, but also common factors of changes in the properties of polymeric materials depending on the amount and nature of the filler.

The object of the research is blends of 21030 polypropylene with «Vistamaxx 6202» and hydrophobized 1TK calcium carbonate with particles size of 2.5 microns (max 20 microns - 1,5%) as the filler. Ethylene-propylene copolymer «Vistamaxx 6202» was used in the composition of polymer material to increase the amount of filler. The following indicators were studied: density, hardness, strength and extension coefficient, melt flow index of PP blends containing «Vistamaxx» to the extent of 0-100 % of mass; calcium carbonate mass content was varied from 0 to 40%. It has been determined that that raising the calcium carbonate content in the polymer blend up to 30% results in increasing the extension coefficient and at the same time in reducing breaking stress; with a subsequent increase of calcium carbonate content in the blend up to 40% the type of the dependencies is changed. The melt flow index for pure polypropylene is 2,5-4 g/10 min, loading it with filler leads to the reduction of melt flow index; raising the filler level in the polymer blend up to 40% results in the increasing of melt flow index almost to the initial value. This proves that the polymer blend of the above mentioned composition can be processed in the traditional for polymers way.

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF TETRAARYLPYRROLE AND DIPHENYLPHOSPHINE OXIDE CONJUGATES

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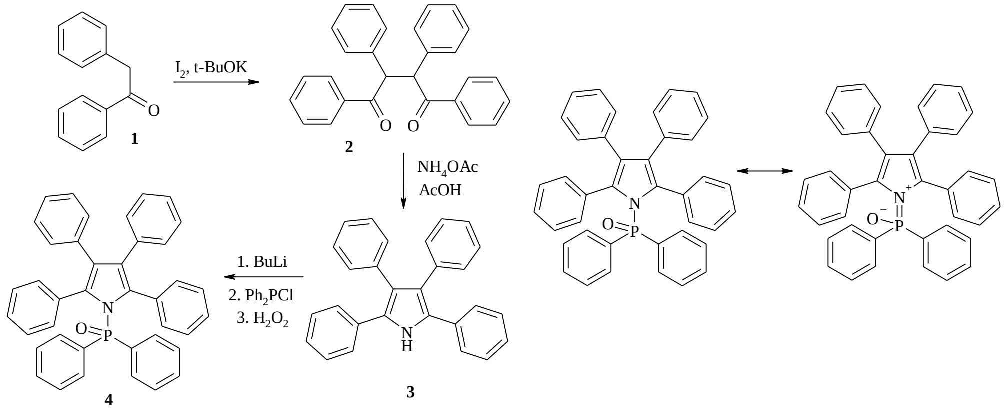
For development of efficient organic light-emitting diodes (OLEDs), both based on TADF emission and on phosphorescence of metal complexes, host materials with the balanced charge mobilities of holes and electrons are required. One of the promising approaches for the synthesis of such materials is based on charge separation inside a molecule by the enhancement of resonance stabilization[1]. With this aim, we synthesized compound **4** by three sequential steps. In the first stage, iodine-promoted oxidative dimerization was accomplished. In the next step, under the standard Paal-Knorr reaction conditions, diketone **2** was transformed to tetraarylpyrrole **3**. Finally, compound **4** was obtained by one-pot procedure.



Density-functional theory calculations were performed for compound **4**. HOMO and LUMO orbitals were found to be well separated and located on donor (tetraarylpyrrole) and acceptor (diphenylphosphine oxide) moieties respectively.

For compound **4** the main photophysical properties were estimated. It exhibited efficient deep blue emission in THF solution (λ_{em} = 426 nm, Φ = 55 %) as well as in solid state (λ_{em} = 416 nm, Φ = 15 %). The dilute solution exhibited single-exponential decay of emission with the lifetime of 3.51 ns. From the low-temperature fluorescence and phosphorescence measurements of the dilute solutions singlet and triplet energy levels were estimated to be 3.5 eV, and 2.6 eV respectively. From the data obtained it can be presumed that compound **4** can be used as host material for yellow and red phosphorescent and TADF-based OLEDs.

Acknowledgements

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SYNTHESIS AND PROPERTIES OF PHOTOCROSS-LINKED POLYMERS OF ACRYLATED SOYBEAN OIL

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Polymeric materials from renewable resources have attracted a lot of attention in recent years. Vegetable oils represent one of the cheapest and most abundant biological feedstocks available in all around the world in large quantities, and their use as starting materials offers numerous advantages, such as low toxicity, biocompatibility, inherent biodegradability as well as certain excellent frictional properties e.g. good lubricity, low volatility, high viscosity index, solvency for lubricant additives, and easy miscibility with other fluids, and more recently in useful polymers and polymer composites [1,2].

The photo-click polymerization of acrylated soybean oil with structurally different dithiols was chosen for this work, because the acrylated vegetable oils represent one of the most abundant annually renewable feedstock available in UV curable materials, and have found numerous applications in paints, varnishes and related materials, whereas the thiol-ene addition reaction, one of the most fascinating “click” reactions in polymer chemistry, has continuously received huge attention owing to its ease of implementation and high efficiency [3].

Two different photoiniciators, 2,2-dimethoxy-2-phenylacetophenone and 2-hydroxy-2-methyl-phenyl-propanone, were tested in different quantities (from 1 to 5 molar %) for the photocross-linking of acrylated soybean oil. Four structurally different dithiols, such as 1,3-benzendithiol, 1,4-benzendithiol, 4,4'-thiobisbenzenethiol and 4,4′*-bis(mercaptomethyl)biphenyl, with* different molar ratios were used in the batches. The curing time ranged from 1 min to 6 min. The best quality films were obtained when 1,3-benzendithiol and (1-3) % of 2,2-dimethoxy-2-phenylacetophenone were used.

The chemical structures of the phtotocross-linked polymers were confirmed by IR spectroscopy. The dependencies of the reological properties, and the density of cross-links of the synthesized polymers on their chemical structure were studied. The thermal, mechanical properties and swelling in different solvents of the photocross-linked polymer film were investigated.

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APPLIANCE OF POLYSACCHARIDES AND ALGINATES IN PRODUCTION OF MEDICAL DEVICES

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Bacterial infection of wounds and burns significantly increases the complexity of the disease or injury. In this regard, the surgical treatment of patients with skin damages, an important place is the local use of various coatings to reduce wound infection, intoxication and speeding terms of epithelialization. To achieve these goals on the woundshould be placed well modeled bandage, it should be atraumatic, provide an opportunity for contactless visual control of the wound, be not toxic and make locally irritating action, be resistant to sterilization, comfortable to wear, easy to use, long term operated on the wound. In addition, it is expected therapeutic effectfrom bandage, and biologically active agentsare injected with that purpose [1].

Traditional textiles are highly effective coating for wounds due to their properties: high sorption capacity, flexibility, adjoining to the surface of complex shape, breathability, lightness, and other valuable qualities. Today bandage development goes towards providing additional medical properties by the injection medecines into a textile material [2].

Therefore noteworthy are coating based on natural or synthetic polymers, those not need to be removed and remain on the wound until resorption of the polymer is completed, or can be removed painlessly, for example with dissolving in water. Of particular interest are the protective coating based on natural hydrocolloid (agar-agar, pectin, carrageenan, starch, cellulose and alginates). Considering the properties of materials (substances) above, alginates attract attention. They along with other hydrocolloids is quite suitable material that can be used to protect the wound surface, namely as the film forming material. They are hygienic and environmentally friendly, in addition, have the ability to bind and remove heavy metals, radionuclides, and certain toxic substances from the human body, purify the digestive system, which is also their positive characteristic [2, 3].

The Department of Applied Ecology, technology of polymers and fibers of Kyiv National University of Technology and Design studies the use of sodium alginate, corn starch, modified starch and Karboksyn - C (Ukraine) for medical membranes. The membranesare created by watering and drying at T ° = 60C. Then studied aqueous solubility, water absorption and physical - mechanical properties. Photocolorimetry method is determined by the solubility of starch components.

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SYNTHESIS AND PROPERTIES OF FLUOROSTYRENE-BASED MONOMERS FOR OPTOELECTRONICS

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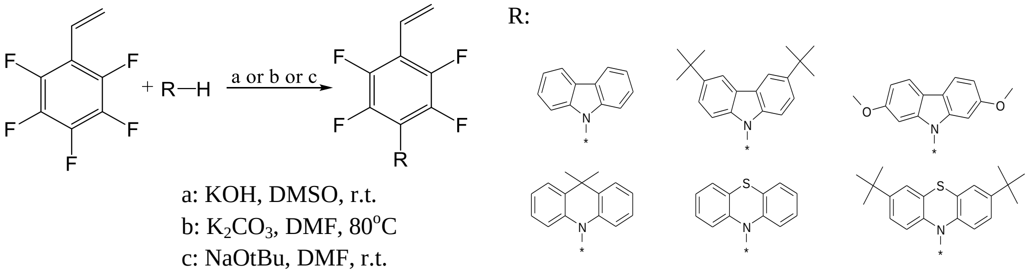
In the past two decades a broad variety of conjugated organic materials exhibiting semiconducting properties was developed for applications in optoelectronic and electronic devices such as organic light-emitting diodes (OLEDs), organic thin film transistors (OFETs), photovoltaic cells, and sensors [1]. The specific features of fluorinated compounds are related to the halogen atom properties such as the high electronegativity, responsible for the strong polarization of the carbon–fluorine bond and for the high bond energy. High thermal and oxidative stability of the fluorinated compounds should lead to the long exploitation time of the devices [2].

In particular, the introduction of electron-withdrawing substituents such as fluorine atoms is expected to lower both the LUMO and HOMO levels in polyconjugated systems facilitating the electron injection. Therefore, fluorinated compounds may play a primary role as active materials in OLEDs and OFETs. They can behave as ambipolar or n-type semiconductors, in contrast to the p-type nature of the corresponding non-fluorinated compounds. [3].

The aim of our work was synthesis of fluorostyrene-based monomers substituted with different electron-donating moieties.



a: KOH, DMSO, r.t.
b: K_2CO_3, DMF, 80^oC
c: NaOtBu, DMF, r.t.

The coumpounds were synthesized through direct nucleophilic aromatic substitution of fluorine atom in pentafluorostyrene. The structures of the synthesized compounds were confirmed by ^1H and ^{13}C NMR spectrometry methods. Thermal, optical and photoelectrical properties were investigated.

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FACTORS AFFECTING SOLVENT-FREE ELECTROSPINNING PROCESS FOR NANOFIBRE PRODUCTION

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Melt spinning of polymers for nanofiber production provides numerous advantages in nanofiber production in comparison with more common solvent electrospinning. The main advantage is skipping the solution of polymer by solvent, which results in no residue or solvent recovery challenges [1]. Therefore, melt spinning has much higher productivity and lower manufacturing costs than solution spinning.

A number of polymers have been used in melt electrospinning. Polymers that have been melt-electrospun include, poly(lactic acid)[2], poly(ethylene glycol)[3-4], polycaprolactone[5], poly(lactide-co-glycolide)[6] and polypropylene[7].

The aim of this study is to research factors affecting the fiber production by a single spinning head melt electrospinning setup, designed and constructed at the Department of Environmental Technology, Kaunas University of Technology. The electrospinning setup consists of high voltage supply, a controlled melting chamber with a needle, and a rotating drum collector (Fig. 1).

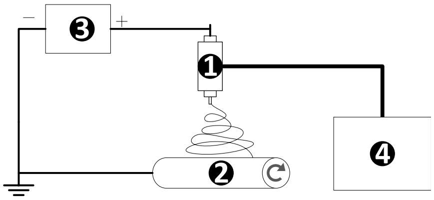

Fig. 1. The scheme of pilot melt electrospinning apparatus (1 – needle with heating mechanism; 2 – adjustable collector; 3 – high voltage DC apparatus; 4 – control panel).

Poly(lactic acid) and Poly(ε-caprolactone) were spun taking into account the tip-to–collector distance, melting temperature, and voltage. Experimental data has been processed by partial least squares regression model implemented in MODDE 10 software (Umetrics AB, Sweden). SEM (FEI Quanta 200 FEG) analysis was used to characterize morphology and diameter of fibers as well as properties of mat. Both polymers were successfully spun at different temperatures, providing a uniformly structured nanofiber mats of adequate mechanical strength. The main challenges of the process included controlling for the nanofiber size in the sub 500 nm range via the adjustments of tip-to-collector distance and voltage between needle and collector.

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ALKYLATION OF ALKOXYBENZENES BY HIGHLY REACTIVE POLYISOBUTYLENE

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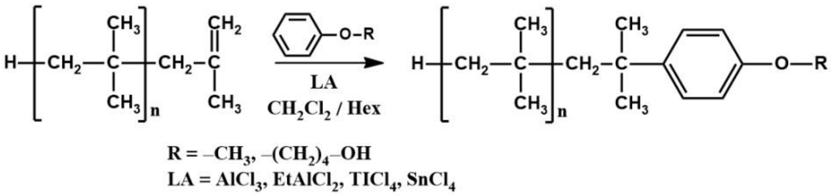
Nowadays, polyisobutylene (PIB)-based materials are widely used due to a combination of its unique properties such as high thermal and chemical stability, low gas permeability and flexibility. Special attention in this area is focused on the synthesis of *exo*-olefin terminated PIBs [1-3]. The injection of various functional groups in PIB allow to modify its properties extending the range of application of PIB as well as to obtain more complexes macromolecular structures.

In this work, the alkylation of alkoxybenzenes (anisole, 4-phenoxy-1-butanol, 2-methoxybenzyl alcohol) by low molecular weight *exo*-olefin terminated PIB using different Lewis acid as catalyst has been investigated (scheme 1). PIB with desired properties (M_n = 1050 g mol^{-1} and ≥85% *exo*-olefin end groups) was synthesized by cationic polymerization as described [3].



Scheme 1. Alkylation of alkoxybenzenes by *exo*-olefin terminated PIB using Lewis acid.

Initially, the effect of the strength of Lewis acid on the efficiency of alkylation was studied using simplest alkoxybenzene – anisole at -40°C. The alkylation reaction proceeds with higher rate in the presence of stronger Lewis acids. However, the using of solid catalysts ($AlCl_3$) is more difficult than liquid or solution of catalyst ($TiCl_4$, $EtAlCl_2$, $SnCl_4$). In addition, the alkylation of 4-phenoxy-1-butanol in the presence of strong Lewis acids is accompanied by side reactions which lead to polymer degradation. It was shown that addition of small amount of water significantly accelerate the reaction when $EtAlCl_2$ and $TiCl_4$ were used. This observation is in agreement with the mechanism of reaction where *exo*-olefin end groups are protonated at the first stage.

The alkylation of 4-phenoxy-1-butanol proceeds much slower than the alkylation of anisole. The best results were obtained using $TiCl_4$ at -80°C. At these conditions PIB alkylated by 2-methoxybenzyl alcohol was successfully prepared and then used as macroinitiator for the synthesis of polyisobutylene-*block*-poly(D,L-lactide).

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POLYSACCHARIDE AND ESSENTIAL OILS COATINGS FOR ACTIVE FOOD PACKAGING MATERIALS

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Active packaging is technology based on the concept of incorporation of certain components into packaging systems that release or absorb substances from or into the packed food or the surrounding environment so as to prolong shelf life and sustain the quality of the food [1]. The serious problem in the food industry consists of protecting shelf-stable food from oxidation reactions. Lipid oxidation causes food quality deterioration including off-odors, off-flavors, color, texture and chemical composition changes. The main strategy to protect the food from oxidation are delivery of antioxidants to the food surface through slow release from the packaging material [2].

In this study, clove oil (CL) or eugenol (EU) containing acrylic component/OSA-starch (AC/S) or cellulose acetate (CA) coatings on corona treated oriented polypropylene (OPP) films were investigated for their possible applications as active food packaging materials. Primarily, the antioxidant properties of the coatings were investigated through the vapor phase by tailored DPPH (2,2-diphenyl-1-picrylhydrazyl) method. The acrylic component/OSA-starch or cellulose acetate coatings containing CL or EU showed high inhibition against DPPH free radicals through the vapor phase (Table 1.)

Table 1. Inhibition of DPPH using different types of coating

No	Type of coating	CL or EU, g/m^2	Inhibition*, %
1	AC/S/CL	0.50 ± 0.05	63.7 ± 3.2
2	AC/S/EU	0.54 ± 0.01	77.0 ± 1.2
3	CA/CL	0.77 ± 0.10	91.6 ± 0.6
4	CA/EU	0.82 ± 0.13	94.1 ± 1.1

* DPPH inhibition trough the vapor phase after 3 h incubation

Eugenol was chosen as most effective bioactive compound for further antioxidant food packaging assay. In this case, AC/S/EU and CA/EU coatings containing different amounts of eugenol (EU=0.32 – 6.40 g/m^2) on OPP film were used to prepare active food packaging materials. Fresh beef samples were packed under modified atmosphere consisting of 80 % O_2 and 20 % CO_2. After 14 days, lipid oxidation of beef kept in active packaging was approx. 2.5 – 3.0 times lower comparing to control sample. Furthermore, beef samples in active packaging showed a good red color stability even after 14 days. It could be concluded that acrylic component/OSA-starch and cellulose acetate coatings containing eugenol have high potential in antioxidant food packaging for fresh meat applications.

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IMMOBILIZATION OF PHENOLIC ACIDS FROM OREGANO EXTRACT ON CATIONIC STARCHES

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Polyphenolic compounds (PH) are usually referred to as a diverse group of naturally occurring compounds containing multiple phenolic functionalities [1]. They occur in variety of dietary and medical plants, and mainly include phenolic acids, flavonoids, coumarins, lignans, stilbenes, quinones, and tannins [2]. These compounds are known to have numerous biological activities such as anti-oxidant, anti-inflammatory, anti-microbial and anti-proliferative. Despite the nutritional benefits, phenolic compounds contribute bitter taste, color, and participate in haze formation [3]. Another important factor in the use of phenolic compounds that should be considered is the presence of unsaturated bonds in their molecular structure which makes them vulnerable to heat, oxygen, light and moisture [4]. So the effectiveness of phenolic compounds depend on preserving the stability, bioactivity and bioavailability of active ingredients. The appliance of encapsulated polyphenols, instead of free compounds, can effectively alleviate these disadvantages.

In current study, the equilibrium adsorption of rosmarinic acid (RA) and lyophilized water extract of oregano (WEO) as RA carrier on cross-linked cationic starch (CCS) with quaternary ammonium groups (DS=0.42) has been investigated at temperatures of 20, 25 and 30 ^{o}C. The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption models were applied to describe the adsorption isotherms of RA.

With the increase of adsorption temperature the values of the Langmuir sorption capacity Q_L and adsorption efficiency EF increased. Meanwhile, the calculated values of Dubinin-Radushkevich adsorption energy E_{DR} confirmed that RA was adsorbed by ion exchange mechanism and values of n_F showed that conditions for RA adsorption on CCS were favourable.

The thermodynamic parameters of the adsorption were calculated. The high negative values of the Gibbs free energy ΔG^o evidenced the great affinity of RA to adsorbent. The positive values of changes of enthalpy and entropy suggested that adsorption was the endothermic process and the order of the system decreased during adsorption.

Acknowledgement

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NEW EFFICIENT 3,3’ – BICARBAZOLE DERIVATIVES FOR LIGHT EMITTING DEVICES: PHOTOPHYSICAL, PHOTOELECTRICAL AND ELECTROLUMINESCENT PROPERTIES

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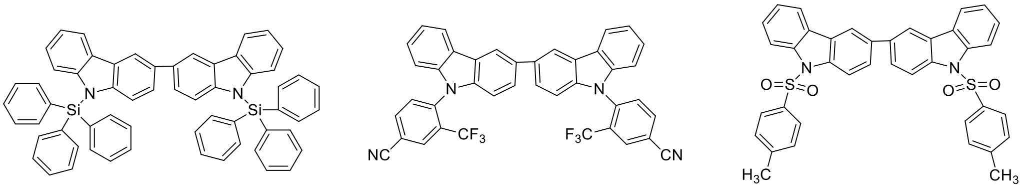
Organic light-emitting diodes (OLEDs) represent one of the most attractive research topics because of the applications for energy-saving solid-state lightning, for flexible and transparent displays. OLEDs are characterized by low drive voltage, high brightness, full-color emission, rapid response, and easy fabrication of potentially large-area, flexible thin-film devices [1].

In this work, we synthesized and studied new functionalized 3,3‘-bicarbazole derivatives after modifications of which three new compounds were obtained: 9,9‘-bis(triphenylsilyl)-9*H*,9‘*H*-3,3‘-bicarbazole (**BiCzSiPh3**), 3-(trifluoromethyl) benzonitrile (**BiCzCF3CN**) and 9,9‘-ditosyl-9*H*,9‘*H*-3,3‘-bicarbazole (**BiCzTos**) (Scheme 1).



BiCzSiPh3 BiCzCF3CN BiCzTos

Scheme 1. Structures of the target bicarbazole compounds

The molecular structures of those compounds were confirmed by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR spectroscopy and mass spectrometry. Optical and photophysical properties were studied by extensive UV-vis and fluorescence spectroscopy, and cyclic voltammetry. The thermal behavior of the synthesized compounds was examined using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

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THE COMPOSITES OF POLY(VINYL ALCOHOL), HORN MEAL AND GLYCEROL AS MULCHING MATERIALS

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In this presentation we report on the preparation of polymer composites from poly (vinyl alcohol), cattle horn meal with high content of nitrogen containing organic substances and glycerol, which is by-product of biodiesel production. The effect of the amount of glycerol as well as of the particle size of horn meal on the mechanical, sorption properties, water vapour permeability, content of water soluble nitrogen and carbon in the films of the composites was studied. The composites were used for the preparation of coatings for the mulching of plants cultivated in pots. The liquid mulching composition was spread out on the surface of the peat substrate. After evaporation of water the polymer coatings, acting as a mulch films, were obtained. It was established that the proposed mulch films retain moisture in the pots and stimulate soil microbial activity. The rate of evaporation of water from the substrate coated with the mulch film was by 26–33 % lower than that from the unmulched substrate. The number of the fungal colony forming units in the substrates depended on the particle size of the horn meal in the mulch composite and were by 1.7×10^4–4.1×10^4 times higher compared with that found in the unmulched substrate. It was established that glycerol present in the composites, prevented *germination* of *weed seeds*. This effect was enhanced with the increase of the amount of glycerol in the mulch composites.

Acknowledgements
Financial support of this research by the Research Council of Lithuania (project No MIP-066/2015) is gratefully acknowledged.

SYNTHESIS OF DONOR-ACCEPTOR STAR-SHAPED CONJUGATED MOLECULES FOR ORGANIC LIGHT-EMITTING DIODES

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Fabrication of OLED devices is one of the most mature and commercially successful applications of organic electronics. Yet increasing the efficiency of OLED emitters remains the central subject of the research in the field. Phosphorescent OLEDs are known for their high efficiency compared to their fluorescent predecessors, however the structure of these materials is limited to the heavy metal-containing organic compounds.

Recently, thermally activated delayed fluorescence (TADF) in purely organic materials has emerged as the alternative way to achieve the internal quantum efficiency close to 100%[1]. TADF characteristics are highly dependent on molecule's structure, therefore the design and synthesis of appropriate compounds as well as the better understanding of structure-property relationships are required.

Conjugated star-shaped molecules are widely applied in the development of organic semiconducting devices and their properties can differ significantly from the linear analogs[2].Truxene with its C_3 symmetry is recognized as a building block for such star shaped structures presenting some interesting optical properties[3].

The most appealing feature of organic electronics for synthetic chemist is nearly unlimited structural diversity of applied materials and extensive possibilities for tuning their properties by chemical modifications. This work in particular is focused on synthesis of star-shaped molecules based on truxene and similar cores and their modification by addition of a variety of donor-acceptor substituents. Possible structure changes required to generate TADF will be discussed as well.

Acknowledgements

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PROPERTIES OF CATIONIC STARCH DERIVATIVES OBTAINED BY REACTIVE EXTRUSION

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In this work cationic starch derivative (CS_{extr}) was obtained by reactive extrusion. The process consists of two stages. In the first one, the mixture of reaction components at the molar ratio starch:2,3-epoxypropyltrimethylammonium chloride:NaOH:H_2O = 1:0.125:0.04:3.5 was made by using reactor (Druvather® Reactor DVT5, Lödige, Germany). In the second one, the obtained mixture was extruded by using twin-screw extruder (ZE25R x 40D UTXi, Krauss Maffei, Berstorff, Germany). The extrusion temperature differs from 90 to 130 °C, screw speed was 50 rpm and the mixture feed rate – about 2 kg/h. The SEM images of CS_{extr} see in Fig.

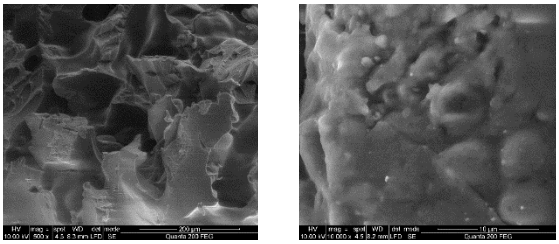

Fig. SEM images of cationic starch obtained by reactive extrusion

The characteristics such as degree of substitution (DS), particle size, swelling power (SP) and solubility index (SOL) of CS_{extr} were evaluated and compared with cationic starch with the same DS value obtained by semi-dry reaction (CS_{gel}) [1]. The flocculation efficiency of cationic starch derivatives were examined and compared with synthetic cationic flocculant (SCF, Unafloc 4963) (Table). The flocculation efficiency was estimated by the minimum flocculant amount (C_{min}) and by the width of flocculation window (W), which shows the range of flocculant doses where the residual turbidity of kaolin suspension upon sedimentation is equal or less 10%.

Table. The characteristics of CS derivatives and the flocculation efficiency

Sample	**DS**	**RE, %**	**SP, g/g**	**SOL, %**	**Particle size**		**Flocculation efficiency**	
					d, nm	**PI**	**C_{min}, mg/g**	**W, mg/g**
CS_{gel}	0.10	90.0	918±66	43±4	$>1\cdot10^8$	-	70.0	96.0
CS_{extr}	0.11	90.4	70±43	76±4	640	0.283	4.4	35.4
SCF	-	-	-	-	-	-	1.7	3.1

Acknowledgements
The authors are grateful to the Research Council of Lithuania for a financial support of the MIP034/14 and the TAP LB-04/15 projects and to the Belarusian Republican Foundation for Fundamental Research.

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INVESTIGATION OF BACTERIAL CELLULOSE BIOFILM STRUCTURE AND PROPERTIES

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Cellulose is the most popular biopolymer in nature. Cellulose is associated with plants but it can be produced by certain type of bacteria as well. BC can be synthesized by bacteria *Gluconacetobacter xylinus*, which is found in fruits, vegetables, vinegar and alcoholic beverages. Chemical structure of BC is the same as that of plant cellulose, but their physical properties are different. BC can demonstrate higher purity and higher degree of crystallinity, high water content (the water absorption is up to 100 %, whereas in the plant cellulose 60 %) [1].

The purpose of this study is to investigate properties of biofilm produced by bacteria fermentation process. Changing medium used for cultivation of biofilm three samples different in properties were produced. In stationary culture conditions bacteria produces thick gel like cellulose film on the surface of liquid medium. BC has porous structure of three-dimensional network of fibrils (Fig. 1).

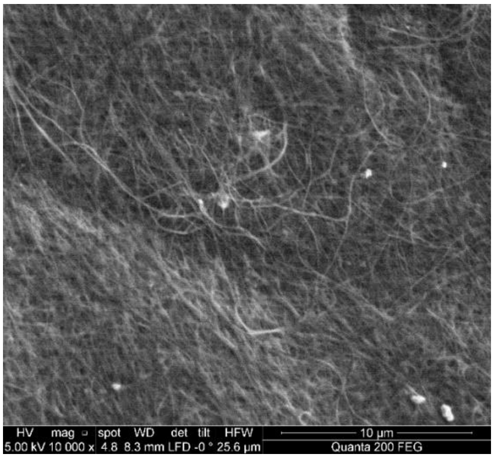

Fig. 1. SEM image of the surface of produced BC biofilm sample

The fibrils of BC are around 100 nm in diameter. The gel like biofilm is characterized by density (0.35-0.92 g/cm^3) and yield (0.15-0.42 g/l). Stable and solid cellulose sheet is produced when gel like membrane is dried. It is estimated that tensile strength of dried biofilm varies from 9.08 MPa to 19.14 MPa when the strain of samples changes from 9.9 % to 34.8 %.

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SYNTHESIS AND STUDY OF GLASS-FORMING MOLECULES COMPRISING ANTHRACENE AND CARBAZOLE/PHENOTHIAZINE MOIETIES

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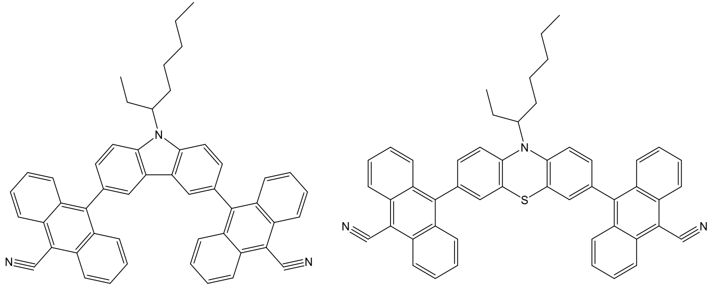
The development of inexpensive, reliable and effective organic electroluminescent materials is one of the hottest research area of organic optoelectronics. Electroluminescence properties of light-emitting materials remain challenging, particularly in terms of easy availability, efficiency, stability and color purity. Thus, it is very important to explore the new class of materials using various synthetic methodologies and starting precursor building blocks. Among potential building blocks, carbazole and phenothiazine have been well known for their excellent thermal stability, charge-transporting properties, versatile structural derivatization, and unique ability to form amorphous films [1,2]. Anthracene is used to construct blue luminescent dyes due to its excellent fluorescent quantum yield, thermal and electrochemical stability, and ease to be modified [3]. In this presentation, synthesis and properties of two novel carbazole- and phenothiazine-based compounds with cyanoanthracene endcaps will be presented.



The derivatives were prepared by C–C coupling reactions of the brominated anthracene and the boronic acids of carbazole or phenothiazine. The chemical structures of the synthesized compounds were confirmed by ^{1}H and ^{13}C NMR, IR and mass spectroscopies. The thermal, optical, photophysical, electrochemical and photoelectrical properties of the synthesized compounds were studied. Compounds were found to possess high thermal stability with the decomposition temperatures exceeding 380 °C, while glass transition temperatures appeared to be as high, as 134 °C and 171 °C for the carbazolyl and phenothiazinyl derivatives, respectively. The impact of structural differences of these bipolar derivatives on the optical, thermal, as well, as electrochemical properties will be discussed in the presentation.

Acknowledgements

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FLOCCULATION MECHANISM BY USING CATIONIC STARCH DERIVATIVES

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The different flocculation mechanism models of the non-sheared and sheared cationic starches (CS) might be suggested. The sheared cationic starch colloidal dispersion consists of the dissolved linear and branched cationic starch macromolecules and of various size CS submicroparticles [1]. By using such a heterogeneous sheared CS composition as a flocculant, many different proccesses / interactions between positively and negatively charged particles might be involved. It is reasonable to suggest that the sheared CS adsorbs onto kaolin particles' surface and then the flocculation is induced due to the electrostatic attraction between the flocculant, already adsorbed onto kaolin particle surface and a bare surface on another particle of kaolin. Dissolved CS macromolecules can easily reach the surface of a kaolin particle adsorb on the outer surface, lie on it flat or penetrate into their pores. For CS submicroparticles, it is more difficult to match the template of kaolin surface charges because of a mismatch in spacing among the cationic groups at CS particle surface and oppositely charged kaolin sites. Depending on CS macromolecules' length: it is short or long, it can induce the flocculation of kaolin suspension by "bridging" or "patch" mechanism models (see Fig. *A* and *B*, respectively). The same theory can be suggested and for CS submicroparticles: the bigger particles can induce the flocculation by "bridging" mechanism, the "bridge" can be form from a particle, and smaller ones can flocculate by "patch" flocculation model (see Fig. *C*).

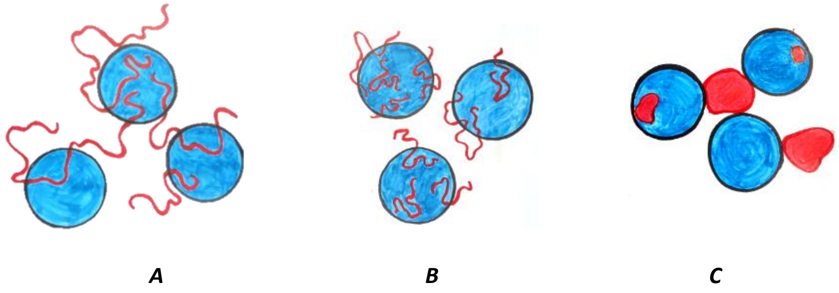

Fig. Models of flocculation mechanism: A – "bridging", flocculant: long CS macromolecules; B – "patch", flocculant: short CS macromolecules; C – "bridging" and "patch", flocculant: CS submicroparticles

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STRUCTURE AND PROPERTIES OF POLYVINYL ALCOHOL / MONTMORILLONITE MULTILAYER FILMS

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Polyvinyl alcohol / montmorillonite film was prepared by layer by layer deposition method. PVOH/MMT film was consisted of polymer and MMT coplanar multilayers. The resulting multilayer film was found to be strong and highly crystalline. Mechanical properties of PVOH/MMT were superior up to 10 times the initial polymer and traditional nanocomposite. Formation of high crystalline polymer and hydrogen bonding interactions between the MMT and PVOH also enhanced the strength and stiffness properties of the obtained PVOH/MMT nanocomposite. It should be noted that the degree of crystallinity was verified by the use of three different approaches: WAXD, DSC, and FT-IR. The received crystallinity values were in the range of 69–85% depending from the used technique.

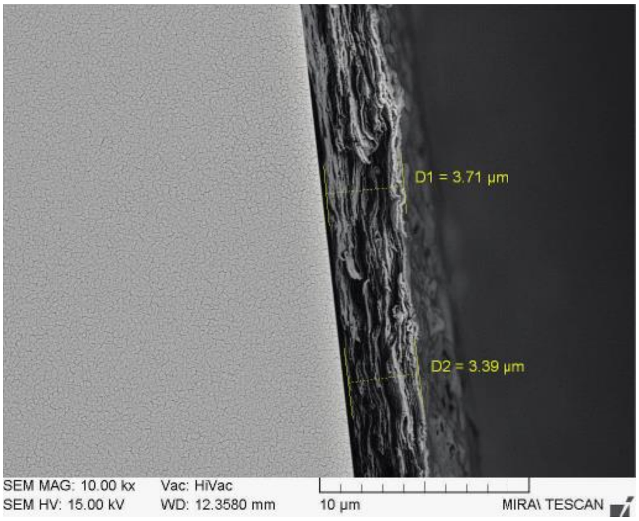

Fig. 1. SEM micrographs of cross section of a 130-double-layer PVOH/MMT film

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SYNTHESIS OF PHOTOSENSITIVE MATERIALS FOR TWO-PHOTON POLYMERIZATION WITH HARD AND ELASTIC SEGMENTS

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As the interest in 3D nano- and micro structuring rises, the requirements for its quality, structuring resolution and speed increases. Polymerization based on two-photon absorption is widely used for manufacturing of various micro functional devices and enables to achieve great spatial resolution with freedom to produce any architectural design desired. One of the applications for those innovative micro structures is scaffold formation to promote stem cell growth for regenerative tissue engineering. Requirements are very high for those kind of structures due to necessity to mimic naturally existing extracellular matrix.

The aim of this investigation was to expand the range of usable prepolymers for scaffold formation with two-photon polymerization. The polymers that are used for this application have to satisfy certain conditions, such as bio-compatibility, low or at least predicted shrinkage, thermal, mechanical and bio- stability.

Due to its suitable properties, polydimethylsiloxane-based polymers show great promise for biomedical applications [1]. Polyurethane synthesis provides possibility to produce polymers with hard and soft segments which leads to unique mechanical properties.

Prepolymers where synthesized by two step process. First, hydroxyl terminated polydimethylsiloxanes (PDMS) were chain extended with different diisocyanates (isophorone diisocyanate, 2,4-toluene diisocyanate, 4,4'-methylenebis(phenyldiisocyanate), 4,4'-methylenebis(cyclohexylisocyanate), 1,6-hexamethylene diisocyanate and 1,3-bis(1-isocyanato-1-methylethyl)benzene). Further chain extension was carried on by the monomers containing hydroxyl group (HEMA and PEGMA) through which they reacted with the end of the polymer chains thus providing photo-reactive groups.

The synthesis of polyurethane prepolymers was observed by ATR FT-IR spectroscopy. The absorption bands corresponding to -NCO groups (2241-2253 cm^{-1}) disappeared during the reaction and new absorption bands corresponding to -NH (~1250 cm^{-1} and ~1550 cm^{-1}), C=C (~1630 cm^{-1}) and C=O (~1740 cm^{-1}) groups appeared in the spectra. Microphase formation and surface morphology were examined by AFM. No clearly distinguished micro-phase structures were observed. Young's modulus of the polyurethane prepolymers was low but about twice higher compared with that of PDMS methacrylate.

It was determined that polyurethane prepolymers were applicable for two-photon polymerization. They displayed promising properties for future applications although further investigation is necessary before implicating those prepolymers to manufacturing.

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PREPARATION AND PROPERTIES OF POLYMER ELECTROLYTE BASED ON POLY(OXYETHYLENE) / NANOCELLULOSE / CARBON NANOPARTICLES COMPOSITES

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Nanocellulose/graphene/carbon nanotubes/poly(oxyethylene) (NC/GR/CNT/PEO) ternary nanocomposites were prepared by solution and melt processing methods. Polymer composite electrolyte was prepared by a blending method with the use of lithium triflate (LiTrf). The morphology, structure, and dielectric properties of the ternary nanocomposites were investigated by dielectric spectroscopy (DS), volume and surface resistivity measurements, X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), calorimetry (DSC) and microscopy (OM). The ionic mobility of the polymer composite electrolytes were measured in the solid and swelled state. Ethylene carbonate (EC), propylene carbonate (PC), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) were used as solvents for the electrolyte preparation and further investigations. The XRD patterns and DSC thermograms testify the polymer crystallinity in the obtained composite electrolyte. The composite electrolyte exhibited the best conductivity properties with the optimum LiTrf content. The spatial network structure developed by the nanoparticles acts as reinforcement for the ionically conductive polymer electrolyte phase. The excellent ion conductivity and storage properties of processed NC/GR/CNT/PEO composites electrolyte indicated their great potential as energy storage material for rechargeable battery application.

FORMULATION OF INKJET INKS MADE OF SEMICONDUCTING POLYMERS

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The ability to print cost-effective electronic components from solutions has opened up many new vistas of applications. Organic materials play a significant role enabling low-cost solution based processing to be adopted for printing on plastic substrates by lowering the process temperature. For printing electronics, varieties of printing techniques are available namely gravure, screen, flexographic, inkjet printing etc. But inkjet printing technique has several unique features like high resolution, drop-on-demand, high-speed and is suitable for mass production. However, printing of organic polymer material through inkjet printer opens new challenges like ink formulation (related to droplets formation), interaction with substrate (wettability) and solvent evaporation control [1-2].

In this communication, we demonstrate method of optimization of formulation of inks based on conjugated polymers suitable for inkjet printing of organic electronic devices like light emitting diodes. Several solvents and their mixture were tested and the concentration of polymer was optimised. The printing was performed on different substrate with modified surfaces e.g. by plasma treatment and with different substrate temperatures. By controlling spreading of the ink on the substrate and the drying conditions, it was possible to obtain thin and continuous layers of semiconducting polymers.

Acknowledgements
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EXCIPLEX AS A KEY FACTOR FOR DEVELOPMENT HIGHLY EFFICIENT WHITE OLEDS

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In the recent years, the development of optoelectronics includes the organic light-emitting devices (OLED). They are characterized by high energy efficiency, good flexibility and low price, compared to other light sources. An urgent task is broadening the electroluminescence spectrum and increasing OLEDs efficiency for application in lighting systems [1]. One of the solution is employing the thermally activated delayed fluorescence (TADF) process, which harvest singlet and triplet excited state [2]. Nevertheless, technological and chemical problems limit the realization of the TADF phenomenon via the single molecule excited state. An alternative to this technology are OLEDs with a minimum number of light-emitting layers that can be achieved by using emission from bimolecular excited species, in particular, exciplex, that are formed by Coulomb attraction between two oppositely charged molecules of different structures with internal quantum efficiency of such system nearly of 100% [3].

In this work, we described new systems based on exciplex emitters, which leads to harvesting the triplet and singlet exciton to increase an efficiency of solid state light system. One of the approaches is mixing of deep blue and orange exciplex emitters. By performing the photophysical investigations we have chosen the appropriate ratio between the donor and acceptor in the exciplex systems which was implemented in the final OLED emissive layer. Moreover, we explored the possible path for variation of the emission colour (from the "warm white" to the white light) by changing intensity of deep blue and orange exciplex emissions.

Acknowledgements
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Donor-Acceptor light emitting
EXCIplexes
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H2020-MSCA-ITN-2015

MANUFACTURING, THERMAL AND MECHANICAL PROPERTIES OF PC/ABS NANOCOMPOSITES WITH LAYERED SILICATES

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Acrylonitrile-butadiene-styrene copolymer (ABS), polycarbonate (PC) and PC / ABS blends are among the most used polymer materials in electronics. It is estimated that the amount of these polymers can form up to 50 % from the total weight of electronic components, thus giving considerable contribution to e-waste. It is not necessary that recycled and virgin polymer materials would show the same properties, but a good balance between properties and processability is absolutely necessary to a recycled material. Use of nanostuctured functional fillers for modification of polymers has gained tremendous popularity in recent years partly due to the possibility of reinforcing a base polymer matrix at minor concentrations of the nanofiller [1–3].

The research has been devoted to the evaluation of the effects of organically modified layered silicates (D43B: montmorillonite, modified with dimethyl-, benzyl, alkyl amine) on the structural and mechanical characteristics of ABS, PC and their binary blends. Virgin and recycled polymers, both, have been used for development of the aforementioned composites. Recycled PC (RPC) has been obtained from post-consumer CDs and DVDs, and recycled ABS (RABS) has been obtained from post-consumer computer parts. ABS content in the investigated composites was 10 wt.%, while the content of nanoclay has been varied in the interval between 0 and 2 wt.%.

By evaluating the effects of nanostructured clay modifier on the tensile stress-strain characteristics of ABS and PC, it has been revealed that for both systems greater modulus and strength increment is observed in the case of the nanocomposites containing 1 wt. % D43B. Besides it has been determined that acceptable recycled polymer content in the polymer blend does not exceed 10 wt. % (in the case of recycled ABS): the material has similar mechanical and thermal properties as virgin polymer mixture. Modification of recycled polymer mixture with nanoclay causes some improvements in mechanical properties such as modulus and strength increment especially in the case of the nanocomposites containing 1 wt. % D43B. Addition of nanostructured clay modifier positively affects also thermal stability of the polymer mixture.

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MECHANICAL AND THERMOSETTING PROPERTIES OF ELECTRON BEAM CROSS-LINKED ETHYLENE-OCTENE COPOLYMER NANOCOMPOSITES WITH MULTI-WALLED CARBON NANOTUBES

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Polyethylene and polyethylene copolymers already for many years have been successfully applied for developing of high energy radiation cross-linked systems having practical applications in various sectors of national economy like building and construction, medicine etc. Metallocene catalyst synthetized polyethylene copolymers, including ethylene-octene copolymers (EOCs), represent the newest generation of thermoplastic polyolefine elastomers. Researches have shown different cross-linking efficiencies of EOCs co-polymers in comparison to low-density polyethylene (LDPE). It has been demonstrated that at lower irradiation doses/exposure times reactivity of EOCs is greater in comparison to LDPE, while at higher irradiation doses/exposure times reactivity of LDPE starts to prevail [1]. Besides, dependence of cross-linking efficiency of EOCs on the octene co-monomer content has been observed; according to Charlesbye-Pinner equation ratio between crosslinking probability and chain scission probability decreases with octene co-monomer content [1]. Considerable increment of modulus of elasticity and strength of EOCs have been observed along with rising irradiation dose, especially at elevated temperature [2]. However, improvement of mechanical performance of the copolymer is limited to irradiation doses of 250 kGy; at higher irradiation doses (500kGy) considerable decrease of mechanical performance has been observed [2]. Recently, carbon nanotubes have found an application in radiation chemistry of polymers contributing to the improvement of mechanical properties of ionizing radiation cross-linked thermoplastic polymers due to resonant structure of graphene layers that may prevent undesired oxidation effects and improve mechanical properties of composites [3].

Consequently, the present study is addressed to investigation of electron beam irradiation effects on the properties of ethylene-octene copolymer (EOC, octene content 17 wt.%) based nanocomposites with (0-15 wt.%) multi-walled carbon nanotubes (MWCNT), developed for heat shrinkable materials. Tensile tests at room temperature and elevated temperature have been performed to determine the temperature-dependent characteristics of elastic modulus and stress-strain behavior on cross-linked EOC in the presence of nanofillers. The dynamic mechanical analysis has been also performed to characterize the viscous-elastic behavior of the developed nanocomposites. Thermomechanical behavior of the irradiated test specimens of EOC/MWCNT compositions, after their preliminary orientation by extension up to 100%, has investigated in the specified temperature range.

The results of the investigation testify that EOC/MWCNT nanocomposites with desired heat shrinkable behavior (thermal relaxation stresses > 0.3 MPa and shrinkage stresses > 0.6 MPa) and improved tensile properties have been obtained. The results of the FTIR analysis confirm that the irradiation induced oxidation of EOC is reduced in the presence of MWCNTs.

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RECYCLED POLYPROPYLENE FOR DEVELOPMENT OF POLYMER NANOCOMPOSITES WITH ZnO

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In average 60 % of thermoplastic polymer materials are recovered nowadays in EU, from which 2/5 are recycled while 3/5 are thermally recovered [1]. Thus there is a great room to expand plastic recycling rates, which becomes especially important by considering ambitious “Zero Plastics to Landfill by 2020” target [2]. An important stimulus to reach this aim is increment of added value of the materials based on secondary polymers. This can be achieved by modifying polymers with nanostructured additives. For an example, ZnO can be used to improve weathering, thermal and mechanical characteristics. Development of nanocomposites on the bases of post-consumer polymers is attractive, however, greatly challenging issue, due to possible impairment of structure and exploitation properties during life cycle of the materials.

In this research following polymer matrices were used: commercial polypropylene PP (Moplen HP456J) and recycled polypropylene RPP (kindly supplied by SIA Nordic Plast). Ethylene-1-octene copolymer EOC (Engage 8200) was used as impact modifier of PP and RPP. Plasma synthesized tetrapod-shaped zinc oxide ZnO nanoparticles (arm length of 70-100 nm and diameter of 10 nm) were synthesized in the RTU Institute of Inorganic Chemistry by plasma torch. Nanocomposites with ZnO have been obtained by melt compounding. Concentrations of the nanofillers have been varied within the range of 0 to 5 wt. %.

By investigating properties of RPP based composites it has been determined that structure of the recycled polymer has been destructed during the life cycle of the primary product, as the result the RPP is characterized by higher melt mass flow rate values and changes in the intensities of carboxyl and hydroxyl absorption bands. It has been determined that by increasing EOC content (up to 30 wt.%) relative elongations at yield and at break as well as impact strength increase. By increasing the content of ZnO in the polymer matrix, in general allows increase tensile and flexural modules of the compositions. By increasing the contents of ZnO and EOC allows increase thermal stability as well as UV weathering resistance of the investigated systems.

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ELECTRONIC, SPECTROSCOPIC AND ELECTROCHEMICAL PROPERTIES OF STAR-SHAPED MOLECULES BASED ON MELAMINE CORE

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Organic π-conjugated molecules are receiving considerable interest due to their potential application in optoelectonic devices such as Organic Light Emmiting Diodes (OLEDs).[1] Among many possible shape of molecules, star-shape presents an interesting option[2,3], usually resulting in improved properties compared to linear analogues.

In this work, a new class of star-shaped derivatives based on melamine core were synthesized and characterized, focusing on the impact of substituent on properties of the molecules. The optical and electrochemical properties of synthesized materials were determined and furthermore simulated with DFT/TDDFT method. Properties of charged forms of investigated molecules (radical cations) were investigated with a spectroelectrochemical methods (UV-Vis-NiR, EPR). Finally, investigated molecules were used as an emitting materials in OLED devices.

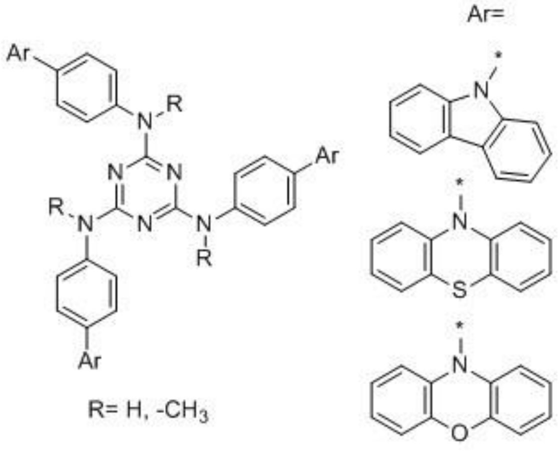

Fig. 1. Structure of investigated compounds

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COPOLYMERS BASED ON BENZOTHIADIAZOLE ACCEPTOR CORE WITH MIXED PYRROLE-THIOPHENE UNITS – ALTERNATIVE FOR ELECTROCOPOLYMERIZATION

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In recent years we can observe growing interest in the field of donor-acceptor type π-conjugated compounds, both low molecular weight and their polymers. An interesting method of obtaining polymers with different electron-donating and accepting groups is so-called electro-copolymerization. This strategy enables fine-tuning of electro- and photo-physical properties of created copolymer without further synthetic effort at the monomer level, furthermore the resultant copolymer may reveal improved electrochemical and optical properties, compared to its homopolymers.[1] However, mayor disadvantage of this method is that it cannot be stated directly what products are obtained at the electrode surface: blends, nanocomposites, interpenetrating networks, or hybrid materials.[2]

To avoid this, we propose the chemical synthesis of monomers containing desired alternate configuration of electron-accepting and electron-donating systems in the main chain of the monomer backbone. This method allows for electro-copolymers with two or even more electron-donating units arranged in strict order in their main chain.

In the work we present electrochemical and spectroelectrochemical properties of multi electron-donating systems coupled with 2,1,3-benzothiadiazole core. It is shown, how change in amount of one electron-donating unit (alkylthiophene or alkylpyrrole) relative to the others in the main chain affects the basic properties of obtained monomers and then their polymers (Figure 1).

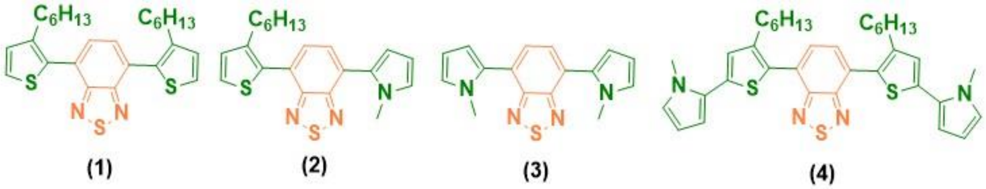

Fig. 1. Investigated compounds

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EXCIPLEX EMITTERS ON THERMALLY EVAPORATED ORGANIC LIGHT EMITTING DIODES USING COMMERCIALLY AVAILABLE MATERIALS

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Organic Light Emitting Diodes (OLEDs) promise to pave the way to the next generation of displays and solid state lighting sources.[1] Since the discovery that excited-state intermolecular charge transfer complexes (Exciplexes) show small energy splitting between singlet and triplet states, efficient Reverse Intersystem Crossing (RISC) can be promoted. This results in an enhancement of the radiative transitions from the singlet state and increasing the device's efficiency. [2–4] By using exciplex structures, devices with E.Q.E.s over 30 % and 10-15% for phosphorescence and fluorescent forming co-hosts, respectively, have been reported with low driving voltage and low efficiency roll-off. [5–7] Nevertheless, the dynamics inside an exciplex formation still needs a more profound study.

This work shines some lights on the exciplex dynamics by exploring the interaction between four commercially available compounds: N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB), 4,4'-(Diphenylmethylene)bis(N,N-diphenylaniline) (TCBPA), 3-(Biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole (TAZ) and 2,2′,2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi). After analysing their photophysical behaviours, and confirming the exciplex formation, the two most promising blends (NPB:TPBi and TCBPA:TAZ) were chosen to produce devices. These OLEDs showed stable performances and E.Q.E.s as high as 2%. Moreover, the concentration dependence between TCBPA and TAZ on the device's emission was studied, leading to optimization on the ratio of the exciplex counterparts.

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Donor-Acceptor Light Emitting
EXCIplexes as Materials for Easy-to-
Tailor Ultra-efficient OLED LIGHTing
H2020-MSCA-ITN-2015/ 674990

INFLUENCE OF AMOUNT AND GRANULOMETRY OF GROUND TIRE RUBBER ON POLYURETHANE-CURED COMPOSITES

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End-of-Life Tires (ELT) are among the largest and most problematic sources of waste, because they capture sizeable land areas, degrade very slowly, contain ZnO, aromatic plasticizers and other components, which are not friendly to environment [1]. If collected, ELT are usually burnt in cement kilns, but such utilization does not yield much added value, so their conversion into Ground Tire Rubber (GTR) gains popularity. GTR is already used to produce running tracks, playground mats, road pavements, but new areas of GTR application, such as insulating materials, are highly welcome [2, 3].

The aim of the present study was to produce composite sheets from GTR and polyurethane binder in order to determine optimal GTR particle sizes and their ratio to the binder. GTR was supplied as truck tread buffings of various sizes by UAB "Devulco". Granulometric sieving showed that the particle size varied from 180 to 2000 μm with 45% between 425 and 850 μm and 30% of 850 to 2000 μm. The composites were produced by initially adding GTR into a beaker and mixing with polyol and diisocyanate. After stirring, the mixture was poured into a curing form and placed into an oven at 60 °C for 4 hours. The obtained specimens were conditioned at the room temperature for 16 hours before measuring mechanical properties.

The produced composite sheets contained from 50% to 90%wt. GTR, while the ratio of diisocynate to polyol was varied from 5:95 to 30:70. Sheet density, ultimate tensile strength, relative elongation, flexural strength at break and Young's modulus were measured. Density of manufactured product changed greatly from 0.5 g/mL to nearly 1 g/mL depending on the amounts of diisocyante, polyol and GTR. The bulk density of GTR itself was measured at 0.432 g/ml, but in the 90% and 60% GTR sheets the density changed from 0.551 to 0.795 g/mL. Reduction of GTR amount from 90% to 70% increased ultimate tensile strength from 0.02 to 1.89 MPa, relative elongation from 22% to 77%, Young‘s modulus increased from 0.055 to 0.207 MPa and flexural strength at break from 0.07 to 0.902 MPa, respectively. An attempt to add glycerol did not improve mechanical properties. The surfaces of composite sheets had sufficiently homogeneous appearance as a result of high amount of fine GTR. Further development of mixing, polyurethane curing and GTR selection methods can result in significant improvement of mechanical properties. Particular attention has to be devoted to the granulometric properties. The early indications suggest that fine rubber sizes lead to much better mechanical properties of the obtained specimens. GTR composite sheets can find an application as insulating material in various industrial segments and increased volume of their utilization can significantly alleviate the problems of ELT recycling.

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF CARBAZOLE-COUMARIN/QUINOLONE CONJUGATES LINKED BY PARA-PHENYLENE SPACER

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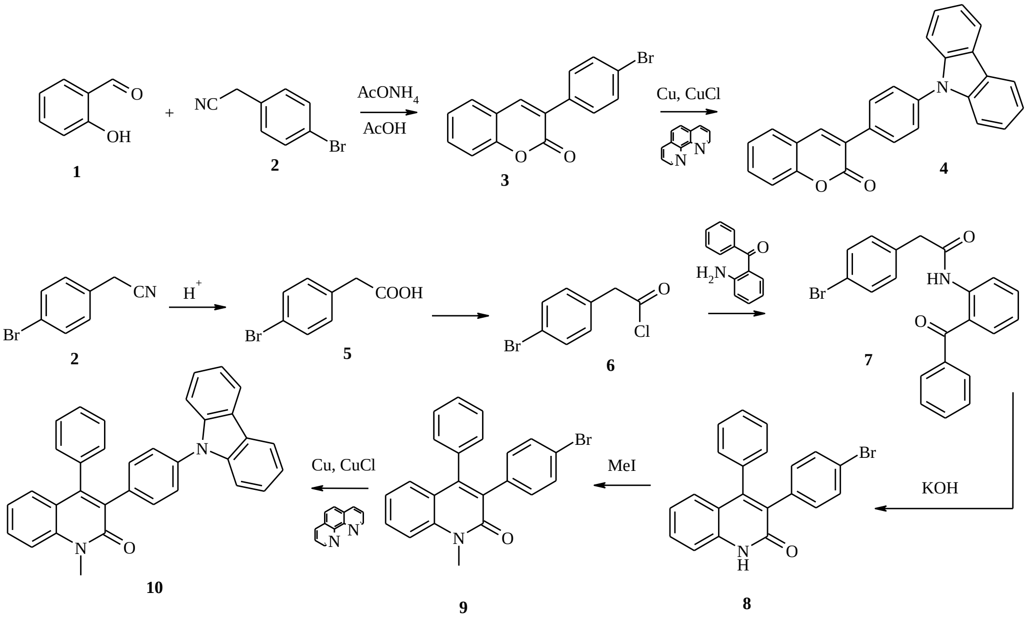
The latest advances in the development of organic light-emitting diodes (OLEDs)[1], solar cells[2], organic lasers and masers[3] are mainly achieved by application of new π-conjugated donor-acceptor materials. Growing demand for such materials requires a bigger database of such compounds and their properties. Taking these circumstances into account, we report in this study on the synthesis and photophysical properties of carbazole-coumarin **4** and carbazole-quinolone **10** conjugates in which chromophores are linked by *para*-phenylene spacer. Synthetic strategy for the preparation of the target compounds included two key points: construction of acceptor cycle and the subsequent Ullmann cross-coupling reaction.



Photophysical properties of the synthesized compounds **4, 10** were studied. In addition, DFT calculations were performed.

Acknowledgements
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ADDITIVE-FREE TRIARYLAMINE DERIVATIVE POLYMERIC HOLE TRANSPORT MATERIALS FOR STABLE PEROVSKITE SOLAR CELLS

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Rapid development of technologies and their influence on people's lives is increasingly associated with energy demand. In order to meet this growing energy demand and minimize related costs new and effective energy generation methods are necessary. Among several alternative sources, photovoltaics are among the most promising, as solar energy is free and inexhaustible energy source. Perovskite solar cells often consist of several layers, each having a specific function and made of materials that meet a certain set of requirements. Some of those requirements include the stability issue, which derives from additives that are used in the process of increasing the conductivity of hole transporting materials.

Having that in mind triarylamine derivative polymers with different functional groups were synthetized as hole transport materials (HTMs) for perovskite solar cells (PSCs). The novel materials enabled efficient PSCs without the use of chemical doping to enhance the charge transport. Devices employing poly(triarylamine) with methylphenylethenyl functional groups showed better power conversion efficiency then widely used additive-free compound - poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA). Notably, devices with the foremost polymer enabled stable PSCs under 1 sun at maximum power point tracking for ~40 hours and under elevated temperature (85 °C) for more than 140 hours. The results present remarkable progress towards stable PSC under real working conditions, which is crucial for industrial application.

GRAPHITE-CARBON-POLYMER COMPOSITES AS PROTECTIVE COATINGS FROM ELECTROMAGNETIC RADIATION

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The ability of different graphite-carbon polymer composites toward interaction with electromagnetic radiation in the microwave frequency diapason was investigated

The composites with different polymer matrix (polyvinyl chloride, polyethylene, epoxy resin, etc.) and various carbon-graphite fillers were prepared and investigated using horn antennas method [1].

The following main carbon-graphite fillers were investigated: 1) colloidal graphite preparation, grade CGP, C0 from Zavalievskii graphite, Ukraine; 2) exfoliated graphite ABG 1010 from Superior Graphite Co., Chicago, IL, USA; 3) graphitized carbon black «PUREBLACK®» from the same producer [2]; 4) technical carbon black PowCarbon 3200F from YongFeng Chemicals Co, Ltd, China; 5) rachislike graphite grade DBX-010 (USA), etc.

Some results of investigations are represented at the Fig. 1a, b.

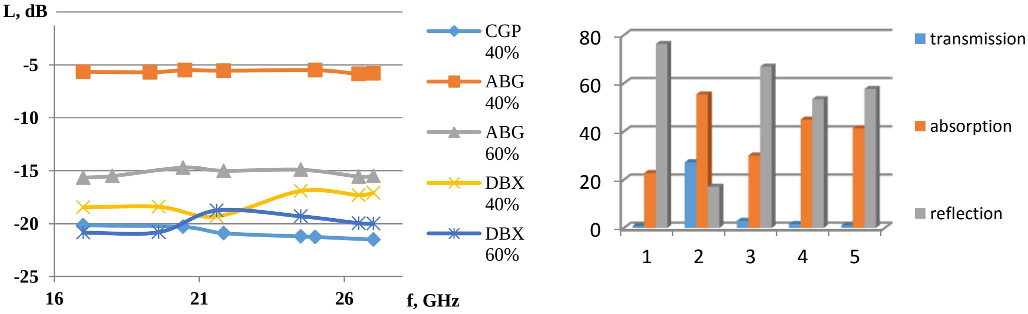

Fig. 1. The comparison of electromagnetic losses for different graphite-carbon materials (a) and their distribution (b). Materials and their content in composition: 1 – CG 40%; 2 – ABG 1010 40%, 3 – ABG 1010 60%, 4 – DBX-010 40%, DBX-010 60%.

Our results have shown that a nature, morphology and content of graphite-carbon fillers make a decisive contribution in the shielding properties of composites. The most effective shielding among the investigated graphite-carbon grades has demonstrated Ukrainian colloidal graphite CGP. For such graphite grade the transmission coefficient is only 0.8% and this effect has achieved mainly due to electromagnetic radiation reflection.

It was shown the possibility to ensure at an average -20…22 dB shielding efficiency in the frequency range 17-27 GHz, very good adhesion to the polymer bodies, simple and not expensive technology of coating preparation using specially prepared paint.

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PROPERTIES OF COLLAGEN-BASED WASTE/POLYETHYLENE THERMOPLASTIC BLENDS

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The current system of using and disposing of plastics has important drawbacks: plastic packaging material with a value of \$80 billion-\$120 billion is lost each year. Aside from the financial cost, by 2050, oceans are expected to contain more plastics than fish (by weight), according to a new report The New Plastics Economy: Rethinking the Future of Plastics [1].

Plastic packaging is present through our everyday life as water drink bottles, microwave dishes, cosmetic containers, rubbish bags, films etc. Polyolefins, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP), constitute the majority of thermoplastics currently used. Considering the fact that consumption and production of those is continuously increasing post-consuming has become an important issue. Polyolefins, as most synthetic polymers, do not decompose naturally. One of the ways of obtaining polyolefine biofragmentable polymers and modify the properties – is incorporating through the blending with polysaccharides, proteins of vegetal and animal origin [2,3]. Such combination allows adjusting the properties of the films, including moisture content, viscosity, strength, organoleptic properties and biodegradation ability. For this purposes chrome free leather wastes can be used.

Leather chrome shavings represent one of the most important by-product of the tannery industry. Chrome containing wastes can be used in the production of non-food items (mulching films, isolation, construction materials, items for the bottom of shoes, leather boards etc.). Conventional leather waste processing is energy and time consuming, therefore utilization by the methods of thermoplastic processing industry remains as one of the solutions.

The research was focused on the preparation of thermoplastic blends based on linear low-density polyethylene (LLDPE) and pre-hydrolyzed collagen (PHC) with ability to biodegradation due to biofragmentation. Blends of LLDPE and PHC, with content up to of 20-50% of PHC, were studied in order to develop a formulation with optimal physical-chemical and mechanical properties.

Proposed technology allows us to adjust conventional equipment of thermoplastic industry processing for collagen-based LLDPE compositions. The technology consists of the following steps: mixing of PHC with LLDPE on z-shaped rotor mixer for 30 min. then drying for 24 hrs. t=90 ^{o}C, homogenizing of dried mixture and injection molding.

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SOLVENT EFFECT ON MOLECULAR CHARACTERISTICS OF MULTIBLOCK COPOLYMERS SYNTHESIZED BY ONE-POT RAFT POLYMERIZATION

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One-pot RAFT polymerization is promising methodology that can lead to precise polymer structures. It is well suited for the synthesis of high-order multiblock copolymers by one-pot sequential monomer addition, where each step is taken to near full monomer conversion without intermediate purification [1, 2]. Block copolymers with functional groups, such as hydroxyl, amine, and thiol groups, have gained increased attention in drug delivery systems, additives and a wide variety of smart materials. Efficient synthetic strategies to these versatile macromolecules remain still a challenge, since functional groups can interact in the polymerization process and cause unwanted side reactions. Solvent effect on propagation rate coefficient in free-radical polymerization is well known. The effect of solvent on RAFT polymerization is more complicated since it is related not only to propagation rate coefficient, but also to chain transfer coefficient, and is studied insufficiently.

In the current work, a series of diblock-, triblock- and pentablock copolymers composed of pHEMA and pBMA blocks, were successfully synthesized via one-pot RAFT technique using stepwise monomer addition approach. Trying to obtain “pure” blocks, polymerization was carried out up to very high conversions (> 95 mol.%), and then the next monomer was added. Triblock- and pentablock copolymers were synthesized in two and three steps, respectively, using difunctional RAFT chain transfer agent (CTA) – di(ethylene glycol) di(2-(1-butyl) sulfanylthiocarbonyl sulfanyl-4-cianopropionate) to ensure chain propagation to two opposite directions. Conversion of the monomers was monitored by ^{1}H NMR spectroscopy, molecular weight of the copolymers was determined by size-exclusion chromatography (SEC) with triple detection.

Polymerizations were performed in a large number of solvents of different nature. The effect of solvents was evaluated by comparing the apparent propagation rate coefficients k_{app} ($k_{app} = k_p \cdot [R^\bullet]$) which were correlated with the dielectric constants of the solvents. The lowest value of k_{app} was in DO ($k_{app} = 3{,}49 \cdot 10^{-5}$ L·mol^{-1}s^{-1}) while the highest in *N*-methylpyrrolidone (NMP) ($k_{app} = 7{,}41 \cdot 10^{-5}$ L·mol^{-1}s^{-1}). The highest dielectric constant is characteristic for DMF ($\varepsilon_{DMF} = 38.25$). Despite slightly lower dielectric constant ($\varepsilon_{NMP} = 32$), NMP was the most efficient solvent. Using NMP as a solvent, conversion of HEMA in the first block was higher than 99%, reaching the degree of polymerization (DP) at about 100 with dispersity of the polymer Đ = 1.16. In the second step, after addition of BMA, conversion of the monomer was ca 95%, DP about 100, and Đ=1.23. In the third step, after repeated addition of HEMA, conversion of the monomer was 96 %, DP about 500 and Đ=1.3. According to the evolution of molecular weight and dispersity, the polymerization seems to be well controlled enabling to get triblock and pentablock copolymers of predetermined structure.

Acknowledgements

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ON THE QUESTION OF DEVELOPMENT OF NEW PHOTO-THERMOPLASTIC CARRIERS BASED ON N-VINYLCARBAZOLE COPOLYMERS FOR THE REGISTRATION OF HOLOGRAPHIC INFORMATION

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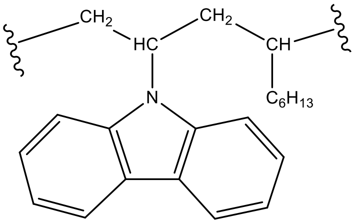
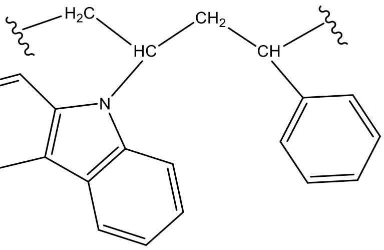
The problem of the development of new photo-thermoplastic carriers (FTPC) for recording holographic information in the red region of the spectrum with the use of photosensitive layers of affordable organic polymers remained relevant to this day. In this regard, were synthesized new copolymers (structures are shown below) of N-vinylcarbazole (N-VC) with 1-octene (OC-1) (I) and copolymers of N-VC with 4-decylstyrene (DS-4) (II).



I. Fragment of copolymer N-VC : OC-1



II. Fragment of copolymer N-VC : DS-4

Both copolymers were synthesized using radical polymerization with initiator azobisisobutyronitrile; concentration of N-vinylcarbazole in copolymers ranged from 60 to 80 mol %. After re-precipitation from methanol, the layers were dried to a constant weight and were used for deposition of photoconductor (PC) layers.

PC-layers were deposited on a metallic base using "spin coating" machine from tetrahydrofuran solutions containing 12 and 15% by weight of photopolymer and 2,4,7-trinitrofluorenone as a sensitizer. The thickness of PC-layers was about 2,0 nm. PC-layers were air dried and in a drying oven at T = 50°C for 1-2 days. The photosensitivity of the obtained layers was controlled using a installation for potential decline. It was established that electro-photosensitivity of PC-layers of N-VC was 2-3 times greater than that of known copolymers of N-carbazolyl ethyl methacrylate PC-layers [1].

For the development of FTPC on the PC-layer was applied a thin layer (0,8-1,0 μm) of thermoplastic of styrene : octyl methacrylate (70:30 mol %).

On the obtained FTPC samples, using holographic equipment, equipped with a laser with a wavelength λ = 0,63 μm, were obtained holographic lattice of relatively good quality with a diffraction efficiency of 10-12%.

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INVESTIGATION OF PHOTOLUMINESCENCE AND AMPLIFIED SPONTANEOUSE EMISSION IN bis-DCM DERIVATES CONTAINING PURE THIN FILMS

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Organic dye solid-state lasers are in nowadays perspective and intensively developing technology in which as laser dyes are widely used different non crystalline structure films forming organic molecules. As all lasers organic dye solid-state laser should consists from two fundamental elements: an active medium and resonator. Compared with traditional inorganic lasers, organic dye lasers are much cheaper and more easily integrated [1].

However, not all organic compounds could be used as laser active medium. One of the decisive factors which allow organic compounds to be used for laser active medium preparation is amplified spontaneous emission (ASE) existence in this compounds.

One of in nowadays in organic solid states lasers widely used laser dyes is well-known red light emitting glass forming organic molecules: 4- (dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) as well as its derivatives.

Previously made experiments with glass forming pyranylidene derivates has shown good luminescence and amplified spontaneous emission properties [2]. Less investigated and not so widely used laser dyes are bis-DCM and its derivatives which could be used in deep red – infrared lasers.

In this work were investigated photoluminescence and amplified spontaneous emission of original bis-DCM derivatives that forms amorphous thin films from solution The difference between the compounds is functional groups attached to donor side of the molecule. These groups are passive bulky groups (assist amorphous state formation) or change electron donor properties.

Neat thin films of investigated compounds on glass substrate were made from chloroform solution by spin-coating method.

Photoluminescence of the samples were excited by continuous wave laser at 405 nm. Photoluminescence quantum yield was measured by the calibrated system Fluorescence spectrometer Pico Master 1 (Photo Med GmbH). Spectral resolution was set to 2 nm. Excitation wavelength was chosen at the absorption maximum for each compound.

ASE was excited by pulse laser at 532 nm. The irradiation area on surface of the sample was stripe form with dimension 3x0.4 mm^2. Light emission was collected at the edge of the sample and measured by spectrometer OceanOptics HR4000.

Photoluminescence and ASE properties of investigated compounds in pure thin films will be discussed.

Acknowledgements

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SYNTHESIS AND CHARACTERIZATION OF NEW ELECTRON-DONOR UNITS FOR EMITTERS

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The prospect of using organic materials for organic light emitting diodes (OLEDs) has flourished for decades since the pioneering work of Tang and Vanslyke in 1980s.[1] It is well known that exciton formation under electrical excitation typically results in 25% of singlet excitons and 75% of triplet excitons. However, 75% of the electrically generated energy is dissipated as heat by triplet excitons in the fluorescence materials, leading to the theoretically highest external quantum efficiency of 5% after considering a light out-coupling efficiency of 20% in device[2]. To increase the efficiency of the OLEDs, many efforts to utilize the non-emissive triplet excitons have been devoted to breaking through the 5% limitation of the OLED device. Among them, thermally activated delayed fluorescence (TADF) was found to have the most rapid progress in recent investigations[3].

Donor-acceptor (D-A) molecular systems with pronounced intra/inter-molecular charge transfer character, are very suitable to realize small singlet-triplet energy splitting through separated HOMO and LUMO for TADF emission without need of heavy metals.

Herein, we designed several of D-A molecules with new electron-donor units, which are expected to form efficient OLED devices. The final D-A materials were synthesized by Suzuki coupling reaction. Their structures were confirmed by the spectral methods. The thermal, electrochemical and photophysical properties of the materials were characterized by thermogravimetric analysis, differential scanning calorimetry, cyclic voltammetry, UV-vis absorption and photoluminescence spectroscopies.

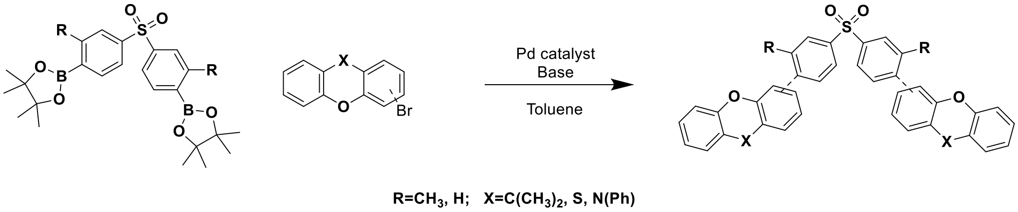

Fig. 1. The general synthesis route of donor-acceptor molecules

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Donor-Acceptor Light Emitting
EXCIplexes as Materials for Easy-to-
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SYNTHESIS OF NEW DONOR-ACCEPTOR MOLECULAR GLASSES AS POTENTIAL TADF EMITTERS

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Organic light-emitting devices (OLEDs) are of current interest from both scientific and practical points of view due to their applications in the next generation full-color flat-panel displays and solid-state lighting sources.[1] In devices, electrically injected charge carriers recombine to form singlet and triplet excitons in a 1:3 ratio. Noble metal based organometallic electroluminescent emitters can theoretically harvest both singlet and triplet excitons, realizing 100% internal quantum efficiencies (IQE); but their further development is hindered due to high cost of noble metals.[2] As an alternative, thermally activated delayed fluorescence (TADF) based on conventional organic aromatic fluorophors, which can also achieve fully excitions utilization through efficient upconversion of non radiative triplets to radiative singlets, has drawn great attention in recent years. Efficient thermally activated delayed fluorescence (TADF) can occur when the energy gap between lowest singlet excited state (S_1 state) and the lowest triplet state (T_1state), ΔE_{st}, is sufficiently small.[3] ΔE_{st} depends largely on the exchange interaction between electrons in molecular orbitals involved in an electronic excitation, it is necessary to control the spatial overlap between molecular orbitals. Thus, the key is design of TADF emitters involves both careful choice of suitable donor and acceptor moieties and small ΔE_{ST}.

In this work we designed and generated a novel emitter with amide synthon (figure 1) as an acceptor for use as an emission materials for OLED. The donor-acceptor-donor (D-A-D) TADF emitter synthesized via cross coupling N-arylation reactions.

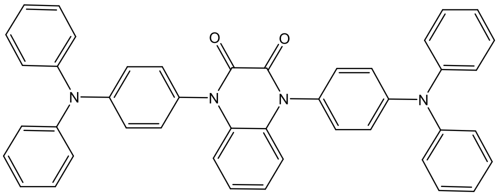

Fig. 1. Structure of D-A-D emitter

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ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL ANALYSIS OF NOVEL TADF EMITTERS

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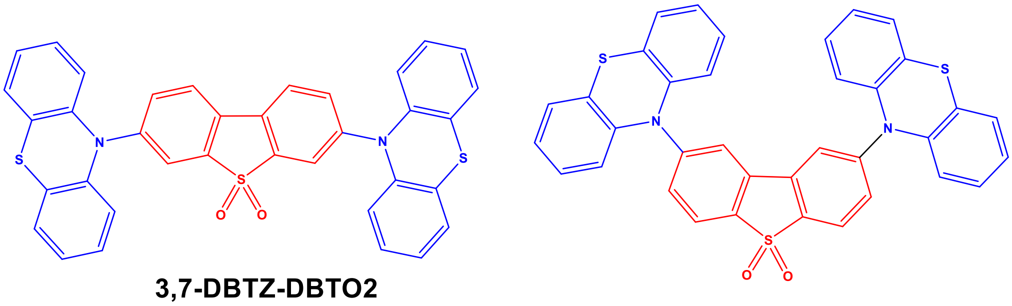
In this study, the effect of the structural properties of two materials, on the efficiency of the thermally-activated delayed fluorescence (TADF) process and resultantly their organic light-emitting diode (OLED) performance has been investigated In order to achieve this goal two isomers, where the electron donor units (PTZ-*Phenothiazine*) are linked in the *2,8* and *3,7* positions of the acceptor unit (DBTO2-*Dibenzothiophenedioxide*) have been chosen as the model systems. These two isomers are of a donor-acceptor-donor arrangement and are called 2,8-DPTZ-DBTO2 (*2,8-di(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene 5,5-dioxide*), and 3,7-DPTZ-DBTO2 *(3,7-di(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene 5,5-dioxide),* respectively. The use of two isomers will allow thorough investigation of how simple structural changes can affect the balance of the reverse intersystem crossing process (RISC) required for efficient TADF. An extensive electrochemical and photophysical study of both of the compounds will show the differences in localization of charge which influence the overall performance of the emitters.



3,7-DBTZ-DBTO2

2,8-DBTZ-DBTO2

Fig. 1. Chemical structure of the molecules 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2.

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