ЕДИНАДЕСЕТА НАУЧНА СЕСИЯ „МЛАДИТЕ УЧЕНИ В СВЕТА НА ПОЛИМЕРИТЕ“

10 септември 2020г.
гр. София

Програма на научната сесия

15:00-15:15ч. Откриване

15:15-16:30ч. Представяне на постери

16.30-16.50ч. Награждаване на отличени постери

16.50-17.00ч. Закриване

Сесията е посветена
на
30 години Институт по полимери

СПИСЪК НА УЧАСТНИЦИТЕ

1. *“Improving the water-repellent and antifungal properties of electrospun cellulose acetate materials by decoration with ZnO nanoparticles”*

Н. Начев, М. Спасова, Н. Манолова, И. Рашков, М. Найденов

Институт по полимери, БАН

Катедра по Микробиология и екологични биотехнологии, Аграрен Университет Пловдив

2. *“Electrospun eco-friendly materials based on PHB and* TiO_2 *prospective for Esca treatment”*

Н. Стоянова, О. Стоилова, М. Спасова, Н. Манолова, Ил. Рашков, М. Найденов

Institute of Polymers, BAS

3. *“Preparation and characterization of novel fibrous materials from polylactide and Schiff base derivative of Jeffamine ED® and 8-hydroxyquinoline-2-carboxaldehyde and its complex with* Cu^{2+}*”*

M. Ignatova, N. Stoyanova, N. Manolova, I. Rashkov, R. Kukeva, R. Stoyanova

Институт по полимери, БАН

Институт по обща и неорганична химия, БАН

4. “Novel polymeric nanosized systems containing biologically active compounds: preparation and antioxidant activity”

S. Kyuchyuk, N. Stoyanova, M. Ignatova, N. Manolova, I. Rashkov

Institute of Polymers, BAS

5. *“Preparation of mixed mesoglobules from cationic termoresponsive copolymers“*

С. Стоилова, К. Иванова, Е. Халаджова, Н. Тончева-Мончева, С. Рангелов

Фармацевтичен факултет, МУ София

Институт по полимери, БАН

6. *“Mixed mesoglobules as platforms for DNA condensation”*

К. Иванова, С. Стоилова, Е. Халаджова, Н. Тончева-Мончева, С. Рангелов

Фармацевтичен факултет, МУ-София

Институт по полимери – БАН

7. *“An approach for preparation of spherical nucleic acids with liposomal cores”*

D. Petkova, E. Haladjova, S. Rangelov

University of Chemical Technology and Metallurgy, София

Institute of Polymers, BAS

8. *“Повърхностно присаждане на аминосъдържащи въглехидрати върху яйчена мембрана за получаване на структура тип "четка". Потенциално приложение за филтър материали.”*

З. Тодорова, А. Бакалова, Д. Динева, Я. Петрова, Н. Косева

Институт по полимери-БАН

9. *“Нови Поликапролактон/полиглицидол блокови и звездовидни съполимери чрез използване на т. нар. "click" химични реакции: Синтез и Охарактеризиране”*

Е. Димитров, Н. Тончева-Мончева, С. Рангелов

Институт по полимери-БАН

10. *“Dual drug loaded mixed micelles for enhanced cancer therapy”*

K. Kamenova, G. Grancharov, B. Tzankov, D. Aluani, V. Tzankova, S. Tzankov, K. Yoncheva, P. D. Petrov

Institute of Polymers, BAS

Faculty of Pharmacy, Medical University of Sofia

Faculty of Pharmacy, Medical University of Pleven

11. *“Nanoparticle diffusion in polymer melts: Molecular dynamics simulations and mode-coupling theory”*

H. Popova, S.A. Egorov, A. Milchev

Institute of Physical Chemistry, BAS

Department of Chemistry, University of Virginia

Institute of Physics, Johannes Gutenberg University Mainz

Leibniz Institut für Polymerforschung Dresden

12. *“Loading of ciprofloxacin into polymeric micelles of different composition”*

R. Stancheva, E. Haladjova, P. Petrov

Institute of Polymers, BAS

13. *“Хибридни хидрогелове на поли(акрилова киселина-съ-акриламид) и магнетит”*

М. Симеонов, А. Апостолов, Е. Василева

Факултет по химия и фармация, СУ

14. *“Нанокомпозитни катализатори от Ni, Co и Mn за алкална електролиза”*

К. Максимова-Димитрова, Е. Лефтерова, Г. Борисов, Е. Славчева

Институт по електрохимия и енергийни системи, БАС

15. *“Електроди за метал-хидрид (МХ) – въздух батерия, съдържащи тефлонизирани въглеродни материали”*

В. Терзиев, Б. Абрашев, Т. Спасов, С. Тодорова, Л. Михайлов, Е. Василева, К. Петров

Институт по електрохимия и енергийни системи, БАС

Факултет по химия и фармация, СУ

16. *“Synthesis and characterization of N- and P- containing triethoxysilanes for modification of mesoporous particles”*

O. Tumurbaatar, H. Lazarova, P. Tuleshkov, M. Popova, P. Shestakova, N. Koseva

Institute of Polymers, BAS

Institute of Organic Chemistry with Centre of Phytochemistry, BAS.

17. *„Thiol-ene coupling reaction achievement and monitoring by in situ UV-irradiation NMR spectroscopy“*

Н. Тончева-Мончева, М. Дангалов, Н. Василев, Х. Новаков

Институт по полимери, БАН

Институт по органична химия с център по фитохимия, БАН

18. *“Alternative approaches for determination of lignin molecular weight”*

D. Nikolova, A. Lederer

Faculty of Chemistry and Pharmacy; Sofia University

Leibniz-Institute for Polymer Research, Dresden

19. *“Биоразградими криогелове получени чрез термично-индуцирано омрежване на 2-хидроксиетилцелулоза с лимонена киселина”*

Н. Бозова, П. Петров

Институт по полимери при БАН

20. *“Hydrogen economy based on advanced materials for hydrogen storage, battery and fuel cell application”*

M. Pandev, M. Slavova, V. Terziev, D. Levi, K. Maksimova-Dimitrova, B. Abrashev

Institute of Electrochemistry and Energy Systems, BAS

Joint Innovation Centre, BAS

21. *“Rapid and initiator-free conjugation of oligonucleotides via UV light-induced thiol-ene click reaction”*

P. Denkova, K. Kostova, E. Dimitrov, N. Toncheva-Moncheva, P. Bakardzhiev, S. Rangelov

Institute of Polymers, BAS

22. *“Пребиотично образуване на хипоксантин от формамид”*

С. Славова, В. Енчев

Институт по обща и неорганична химия, БАН

23. *“Thermoresponsive properties and levofloxacin loading capacity of star shaped poly(N-isopropylacrylamides)”*

S. Bozhilova, S. Ivanova, D. Christova

Институт по полимери, БАН

24. *“Изследване потенциала на различни PEO-PCL мицелни системи за разтваряне на хидрофобни биологично активни вещества.”*

В. Кортенова, М.-Д. Атанасова, Г. Грънчаров, Г. Добриков, М. Шрьодер, И. Угринова, Д. Момекова, П. Петров

Факултет по химия и фармация, СУ

Институт по полимери, БАН

Институт по ОХ с Център по фитохимия, БАН

Институт по молекулярна биология, БАН

Фармацевтичен факултет, МУ София

25. *“Novel photoactive polymer coatings: properties and antibacterial activity”*

N. Filipova, N. Georgiev, I. Lalov, R. Bryaskova

University of Chemical Technology and Metallurgy, Sofia

26. *„Design of PEG-modified magnetic nanoporous silica based miltefosine delivery system“*

I. Trendafilova, H. Lazarova, M.Popova, N. Koseva, V. Mitova, J. Mihály, D. Momekova, S. Konstantinov, Á. Szegedi

Institute of Organic Chemistry with Centre of Phytochemistry, BAS

Institute of Polymers, BAS

RCNS, Institute of Materials and Environmental Chemistry, Budapest, Hungary

Faculty of Pharmacy, MU Sofia

27. *“Synthesis and photocatalytic investigations of macrocyclic oligomer/polystyrene/TiO2/CeO2 composite”*

S. Dimova, K. Zaharieva, F. Ublekov, I. Stambolova, M. Todorova

Институт по полимери, БАН

Институт по катализ, БАН

Институт по обща и неорганична химия, БАН

Химикотехнологичен и металургичен университет, София

ПОСТЕРИ

Постер 1

Improving the water-repellent and antifungal properties of electrospun cellulose acetate materials by decoration with ZnO nanoparticles

Nasko Nachev[1], Mariya Spasova[1], Nevena Manolova[1], Iliya Rashkov[1] and Mladen Naydenov[2]

[1]*Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, bl. 103A, BG-1113 Sofia, Bulgaria,*

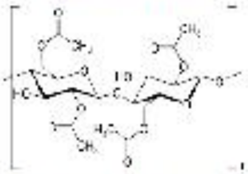
[2]*Department of Microbiology, Agricultural University, BG-4000 Plovdiv, Bulgaria*

In the recent years, electrospinning is considered as one of the most perspective and effective technologies for the fabrication of continuous polymer fibers having micro- and nanoscale diameters and length reaching several meters. Cellulose acetate (CA) is one of the most important esters of cellulose. The advantages of CA are its low cost, ease of solubility in solvents suitable for electrospinning, facile production and wide variety of applications. ZnO is nontoxic and exhibits photochemical and antibacterial activity. The aim of the present study was to prepare electrospun materials (beads or fibers) from cellulose acetate or cellulose acetate decorated with ZnO with improved water-repellent and antifungal properties.

Materials

Cellulose acetate (CA)

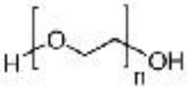
Mn = 30 000 g/mol



Biodegradable, biocompatible, nontoxic

Polyethylene glycol (PEG)

Mr = 1,800–2,200 g/mol



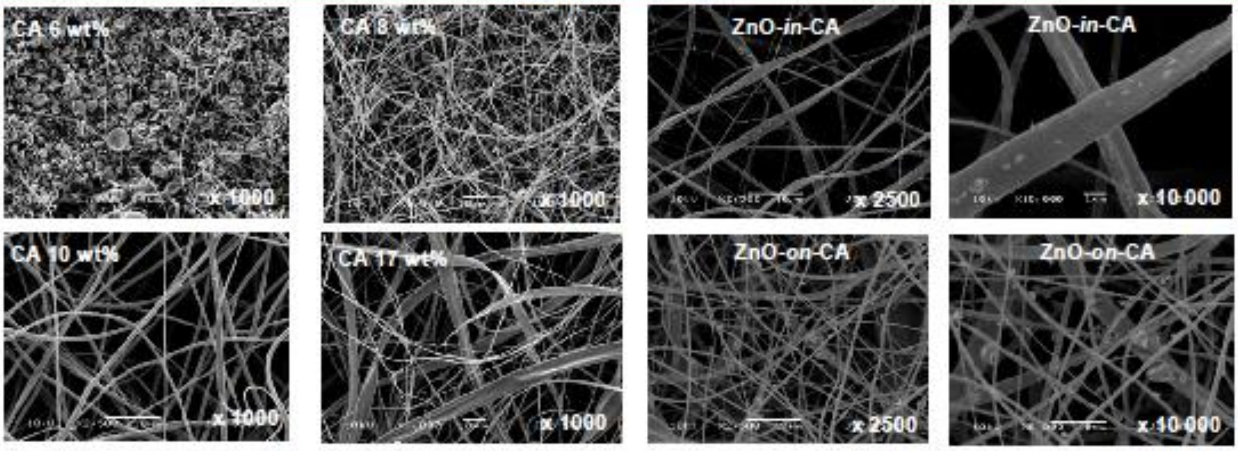
Biocompatible, nontoxic

Zinc oxide (ZnO)

Nontoxic with photochemical and antibacterial activity

Set-up

SEM micrographs



Water contact angle

CA mat

ZnO-*in*-CA mat

ZnO-*on*-CA mat

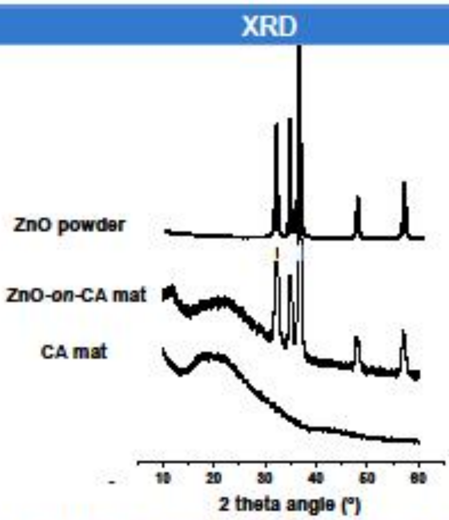
Antifungal activity

control

ZnO-*in*-CA mat

ZnO-*on*-CA mat

XRD



Conclusion. CA fibrous materials and CA/ZnO hybrid materials have been successfully prepared by conjunction of electrospinning and electrospraying techniques. It was found that the concentration of the spinning solutions/dispersions influenced the morphology of the obtained particles/fibers. The incorporation of ZnO nanoparticles imparted superhydrophobic and antifungal properties to ZnO-*on*-CA mats. These features indicate that the obtained hybrid fibrous materials could find application in agriculture for plant protection against adhesion and growth of pathogenic fungi.

Acknowledgement: **Financial support from the Bulgarian National Science Fund (Grant KP-06-OPR03/2) is gratefully acknowledged.**

Постер 2

Electrospun Eco-Friendly Materials Based on PHB and TiO_2 Prospective for Esca Treatment

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I. Raskhov, M. Naydenov
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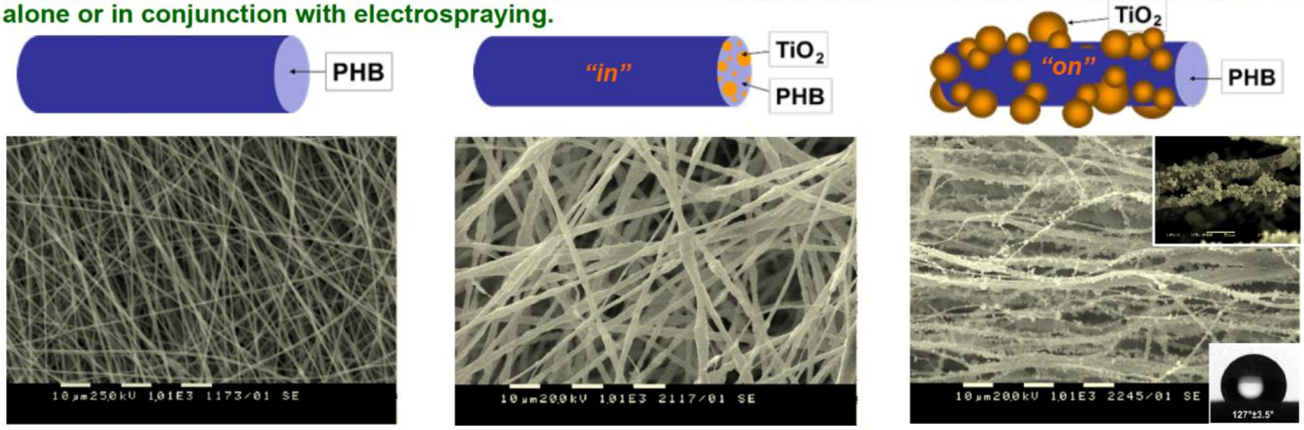
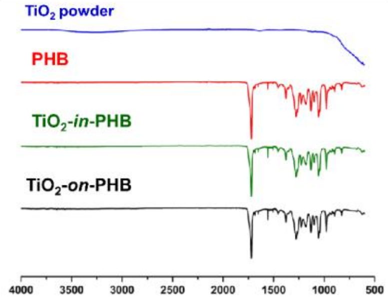
Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, 1113 Sofia

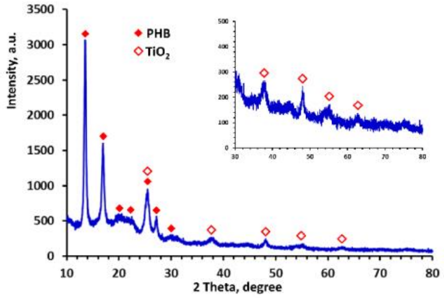
Esca is a disease of grapevines that causes trunk damage and entire-plant wilting. *Phaeomoniella chlamydospora* is one of the main fungi causing Esca. The aim of the present study was to obtain eco-friendly materials with potential antifungal activity against *P. chlamydospora* based on biodegradable and biocompatible poly(3-hydroxybutyrate) (PHB), nanosized TiO_2 (nanoTiO_2), and chitosan oligomers (COS).

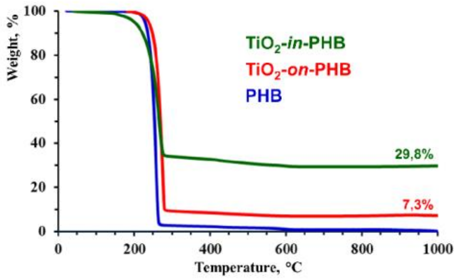
Fabrication and Characterization of Fibrous Composite Materials

Two types of fibrous materials based on PHB and nanoTiO_2 (anatase) were fabricated by electrospinning alone or in conjunction with electrospraying.





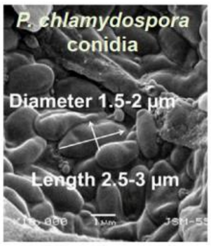


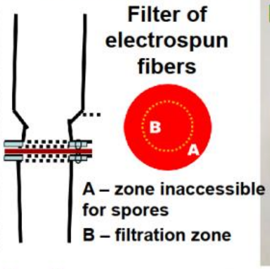


No interaction between PHB and nanoTiO_2 was detected in the FT-IR spectra of fibrous materials. Characteristic diffraction peaks of TiO_2 (anatase) and PHB were detected in the XRD spectra. The residual weight determined by TGA was close to the weight of TiO_2 in the feed.

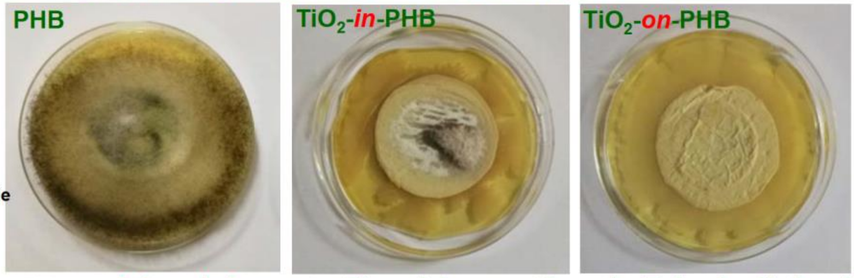
Antifungal activity of the fibrous materials against *P. chlamydospora*

The higher roughness of the TiO_2-*in*-PHB and TiO_2-*on*-PHB fibrous materials led to more difficult passage of the conidia through them and resulted in a higher filtration efficiency compared to the PHB. The TiO_2-*on*-PHB fibrous material that contacted with *P. chlamydospora* during filtration experiment showed complete inhibition of the growth of the fungi remaining in the fibrous material after the filtration.





A – zone inaccessible for spores
B – filtration zone



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Acknowledgements: Financial support from the Bulgarian National Science Fund (Grant КР-06-OPR03/2) is gratefully acknowledged.

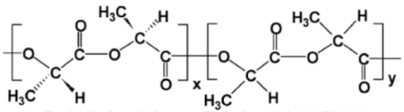
Preparation and characterization of novel fibrous materials from polylactide and Schiff base derivative of Jeffamine ED® and 8-hydroxyquinoline-2-carboxaldehyde and its complex with Cu^{2+}

M. Ignatova[1], N. Stoyanova[1], N. Manolova[1], I. Rashkov[1], R. Kukeva[2], R. Stoyanova[2]
[1]Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev St, Bl. 103A, BG-1113 Sofia, Bulgaria; [2]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St, Bl. 11, BG-1113 Sofia, Bulgaria

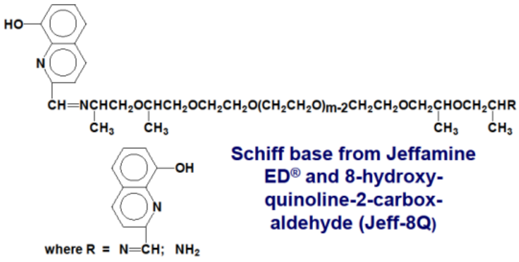
Aim

8-hydroxyquinoline and its derivatives are well known for their high antimicrobial, antioxidant and antitumor activity. It is assumed that their biological activity is related to their chelating ability against transition metal ions (Cu^{2+}, Fe^{2+}, Fe^{3+}, etc.) of biological importance. The incorporation of these biologically active compounds in electrospun non-woven textile can impart favorable biological properties to the textile. The present study is aimed at the preparation of fibrous mats of polylactide (PLA) containing a Schiff base from Jeffamine ED® and 8-hydroxyquinoline-2-carboxaldehyde (Jeff-8Q) or its complex with Cu^{2+} (Jeff-8Q.Cu^{2+}) of various designs by applying one-pot electrospinning or electrospinning combined with dip-coating. The coordination of Cu^{2+} in Jeff-8Q.Cu^{2+} -containing fibrous materials was studied by EPR spectroscopy.

Materials



Poly(L-lactide-*co*-D,L-lactide) (PLA)

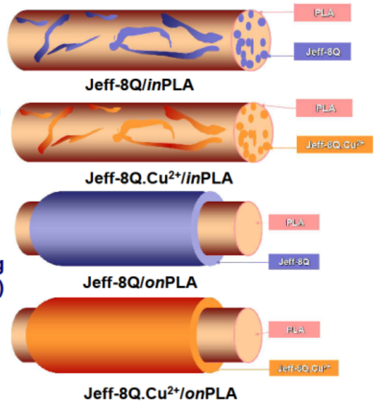


Schiff base from Jeffamine ED® and 8-hydroxy-quinoline-2-carbox-aldehyde (Jeff-8Q)

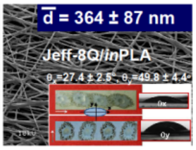
Schematic representation of fibers

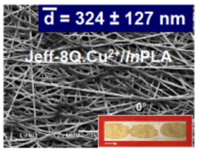
type *"in"* (one-pot electrospinning)

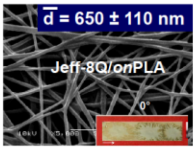
type *"on"* (electrospinning and dip-coating)

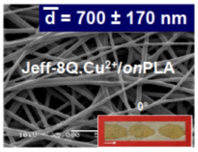


SEM micrographs

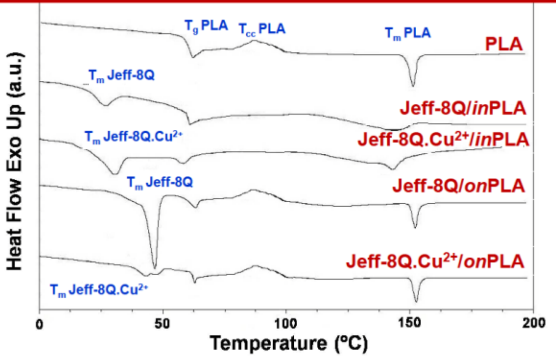






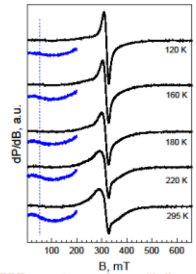


DSC thermograms

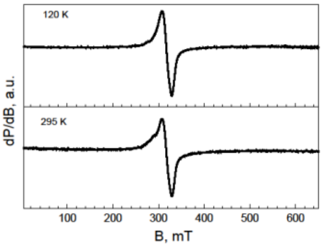


Study of the coordination of Cu^{2+} ions in Jeff-8Q.Cu^{2+}-containing mats by EPR spectroscopy

EPR spectra of Jeff-8Q.Cu^{2+}/*in*PLA mat

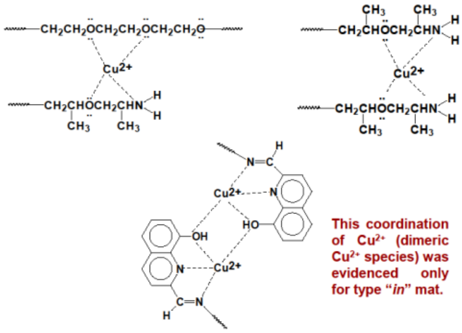


EPR spectra of Jeff-8Q.Cu^{2+}/*on*PLA mat



The EPR spectrum of type "in" mat consisted of at least two overlapped signals - a broad signal (180 K-295 K) and a low intensive signal appeared at weak magnetic fields (blue line). The EPR spectrum of type "*on*" mat contained only one slightly asymmetric signal with a *g*-factor and line width, which matched those observed at type "*in*" mat.

Schematic representation of coordination of Cu^{2+} in types "*in*" and "*on*" mats



This coordination of Cu^{2+} (dimeric Cu^{2+} species) was evidenced only for type "*in*" mat.

CONCLUSIONS: For the first time Jeff-8Q- or Jeff-8Q.Cu^{2+}-containing fibrous materials of various design were prepared. To achieve this, one-pot electrospinning or combining electrospinning and dip-coating were applied. The performed EPR analyses showed intra- and intermolecular coordination of Cu^{2+} with O- and N-atoms of Jeffamine moieties of the fibers. In Jeff-8Q.Cu^{2+}/*in*PLA mats the 8Q moieties bridged Cu^{2+} ions into dimeric [Cu^{2+}-8Q] complexes. In the case of type "*on*" mats only the coordination of Cu^{2+} ions with Jeff in Jeff-8Q chains of the fibers was evidenced.

Acknowledgements: Financial support from the Bulgarian National Science Fund (Grant KP-06-N39/13/2019) is kindly acknowledged.

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NOVEL POLYMERIC NANOSIZED SYSTEMS CONTAINING BIOLOGICALLY ACTIVE COMPOUNDS: PREPARATION AND ANTIOXIDANT ACTIVITY

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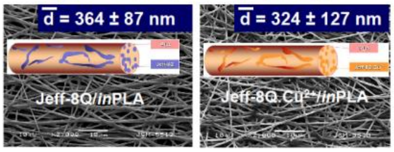
Akad. G. Bonchev St, Bl. 103A, BG-1113 Sofia, Bulgaria

Aims: To prepare polymeric nanosized systems (electrospun nanofibers and nanoparticles) containing biologically active compounds (Schiff base from Jeffamine ED® and 8-hydroxyquinoline-2-carboxaldehyde (Jeff-8Q), its complex with Cu^{2+} (Jeff-8Q.Cu^{2+}) and berberine chloride (Brb)) with antioxidant activity. To explore the effect of the composition of the obtained nanosized materials on their antioxidant properties.

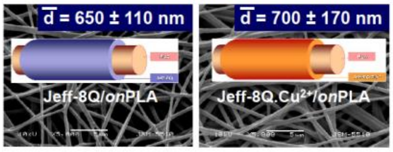
Preparation and antioxidant activity of Jeff-8Q- and Jeff-8Q.Cu^{2+}-containing fibrous materials

SEM micrographs

type "*in*" (one-pot electrospinning)

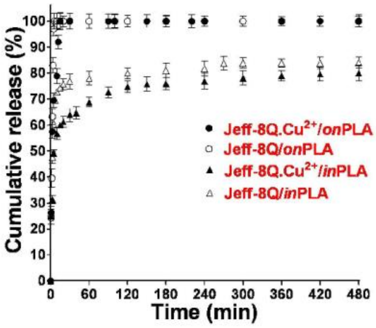


type "*on*" (electrospinning and dip-coating)

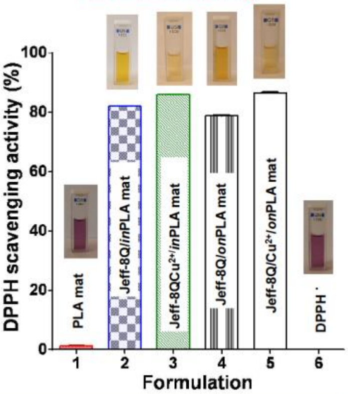


In vitro release profiles

PBS (pH 7.4), 37 °C

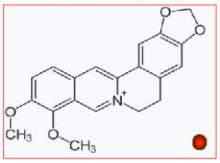


Antioxidant activity

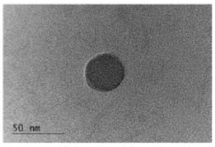


Preparation and antioxidant activity of Brb-containing nanoparticles

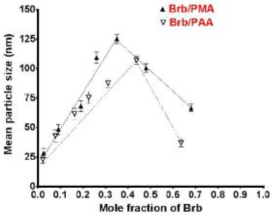
Structure of berberine chloride (Brb)



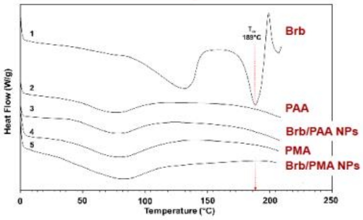
TEM micrograph of Brb/PAA NPs



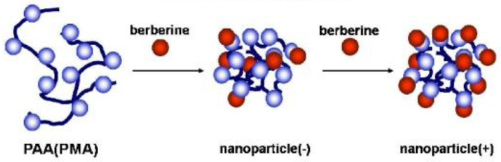
Mean size



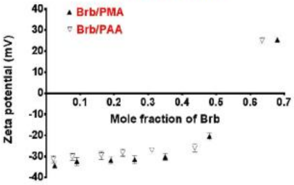
DSC thermograms



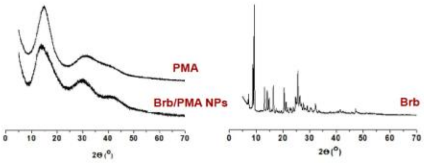
Schematic representation of the preparation of Brb/PAA (PMA) NPs



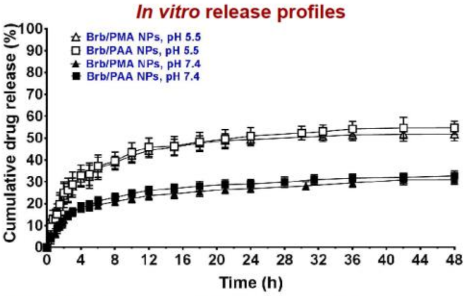
Zeta potential



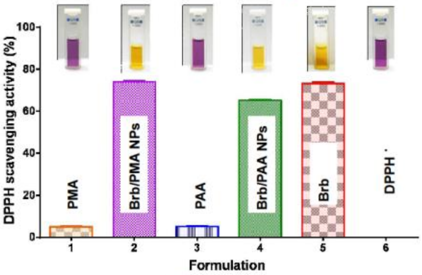
XRD analyses



In vitro release profiles



Antioxidant activity



CONCLUSIONS: Novel Jeff-8Q- or Jeff-8Q.Cu^{2+}-containing nanofibrous materials and Brb-containing nanoparticles were prepared. The Brb incorporated in the Brb/PMA (PAA) NPs was in the amorphous state, which is favorable for use as a drug dosage form. It was found that the *in vitro* release of Jeff-8Q (Jeff-8Q.Cu^{2+}) from the type "*on*" mats was more rapid than that of the type "*in*" mats. The Brb release profile was pH-dependent. Jeff-8Q-, Jeff-8Q.Cu^{2+}- and Brb-containing nanosized materials displayed high antioxidant activity.

ACKNOWLEDGEMENTS Financial support from the Bulgarian National Science Fund (Grant KP-06-N39/13/2019) is kindly acknowledged.

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PREPARATION OF MIXED MESOGLOBULES FROM CATIONIC TERMORESPONSIVE COPOLYMERS

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INTRODUCTION

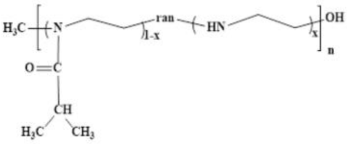
Mesoglobules are colloidally stable and typically nanosized particles which are formed in dilute aqueous solution of thermosensitive polymers upon heating above certain critical temperature. These particles are of considerable interest for drug and gene delivery. Whereas the scientific literature for mesoglobules prepared from copolymers comprising thermosensitive moieties is huge, only few studies for preparation of mixed mesoglobules are present.

In this contribution we report on the preparation and physicochemical characterization of mixed mesoglobules obtained from two cationic thermosensitive polymers. Positively charged mesoglobules of different compositions were prepared by applying two heating protocols – gradual and abrupt heating. Their properties were investigated by dynamic and electrophoretic light scattering.

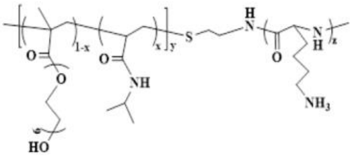
COPOLYMERS

Copolymers comprising thermoresponsive moieties based on PNIPAM or PIPOX and hydrophilic cationic moieties based on PLL or PEI were used. PNIPAM and PIPOX are structural isomers, therefore, we expected their mixing during aggregation. The PLL and PEI moieties of copolymers were expected to provide positive charges of the particles.

Copolymer	Code	Mn g/mol	Cationic content, %
PNIPAm-PEG-PLL$_{37}$	PLL37	20 800	30
PNIPAm-PEG-PLL$_{10}$	PLL10	15 200	10
PIPOX-PEI	PEI	7 300	50



poly(2-isopropyl-2-oxazoline)-ran-polyethylenimine
PIPOX-PEI

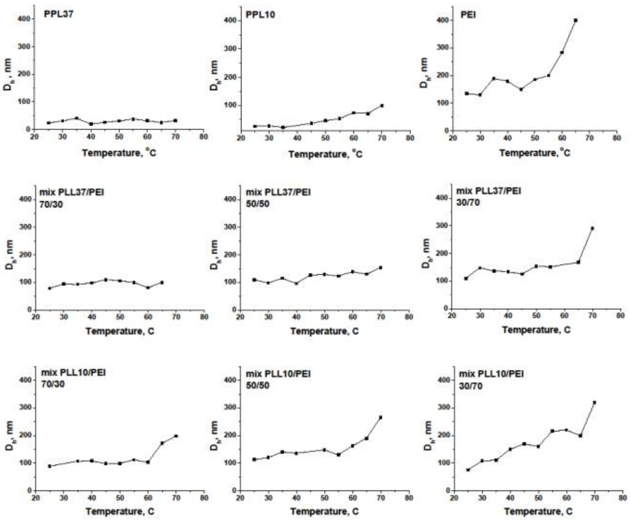


poly(N-isopropylacrylamide)-graft-poly(ethylene glycol)-b-poly(L-lysine)
PNIPAm-PEG-PLL

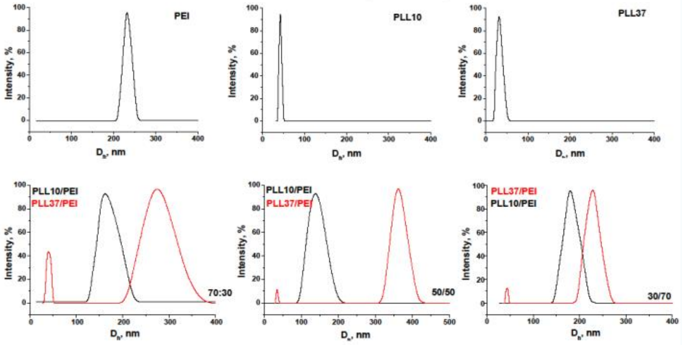
PREPARATION OF MIXED MESOGLOBULES

Mixtures from PLL and PEI based copolymers were used in three weight ratios: 70/30, 50/50 and 30/70. The aqueous solutions of the mixtures were prepared at a 0.5 g.L^{-1} total concentration. The solutions were kept at 4 °C prior to use. The behavior of neat polymers was investigated for comparison. Two heating rate protocols (gradual and abrupt) were used. Gradual heating was performed as the copolymer solutions as well as their mixture were heated from 20 to 80 °C with heating rate of 5 °C/min. The phase transition was followed by the changes in the scattering intensity and respectively by the hydrodynamic diameter, D_h, of the aggregates. Abrupt heating was achieved as the copolymer solutions were abruptly heated at 70 °C. The formation of mixed mesoglobules was evaluated from the size distribution curves and ζ potential values.

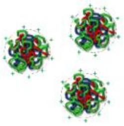
Gradual heating



Abrupt heating



Sample	Z potential, mV
PLL10	31.4
PLL10/ PEI 70:30	28,16
PLL10/ PEI 50:50	27.4
PLL10/ PEI 30:70	24.6
PEI	18.4



CONCLUSION

The ability of PNIPAm-PEG-PLL and PIPOX-PEI termoresponsive copolymers to form cationic mixed mesoglobules was investigated. When gradual heating was applied the particle dimensions were found to increase with temperature for PLL10/PEI mixtures at all of the investigated ratios. In contrast, when PLL37 was used changes in D_h was observed only at the 30/70 weight ratio. In addition, upon abrupt heating PLL37/PEI mixtures exhibited bimodal size distributions with the first maximum close to that of pure PLL37. On the contrary, PLL10/PEI mixtures resulted in monomodal size distributions with dimensions different from those of pure mesoglobules indicating successful mixing of both copolymers. The decrease of ζ potential with PEI content was another indication for formation of mixed mesoglobules of PLL10 and PEI. The resulting cationic mixed mesoglobules presumably possessed a mixture of primary and secondary amines on their surface, therefore, they were considered promising as gene delivery vehicles.

Acknowledgements: This work was supported by the Bulgarian Ministry of Education and Science (Grant D01-217/30.11.2018) under the National Research Programme "Innovative Low-Toxic Bioactive Systems for Precision Medicine (BioActiveMed)" approved by DCM # 658 / 14.09.2018

MIXED MESOGLOBULES AS PLATFORMS FOR DNA CONDENSATION

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INTRODUCTION

Polyplexes are promising non-viral gene delivery systems. The polyplex formation is based on electrostatic interactions between synthetic polymers or polymer particles and DNA. A necessary prerequisite for the polymer partner is the presence of positively charged groups in the polymer chain such as amino groups. However, the type of the amino group (primary, secondary, tertiary) has been found to be essential for DNA/polymer interactions as well as for further biological relevance of the resulting complexes. The primary amino groups are known to possess high binding affinity and to form stable complexes with DNA, but they are usually associated with high toxicity. The secondary and tertiary amines are able to protonate to varying degrees depending on the pH of the medium and are responsible for the successful endosomal escape and transfection efficiency.

In this work positively charged mixed mesoglobules were used as platforms for DNA condensation. They were formed from poly(N-isopropylacrylamide)-graft-poly(ethylene glycol)-b-poly(L-lysine), PNIPAm-PEG-PLL, and poly(2-isopropyl-2-oxazoline)-ran-polyethylenimine, PIPOX-PEI, copolymers upon heating at temperatures well above the transition temperatures of the thermosensitive moieties. The mixed composition of mesoglobules ensured different primary to secondary amine ratios that could be important for the whole process of DNA binding, delivery, and release. The complexation ability of mixed mesoglobules was investigated by dynamic and electrophoretic light scattering.

MIXED MESOGLOBULES

Mesoglobules were formed from PNIPAm-PEG-PLL and PIPOX-PEI cationic polymers containing thermoresponsive moieties at three different weight ratios: 70/30, 50/50 and 30/70. They were prepared at total concentration of 0.5 mg/ml by abrupt heating protocol at 70 ºC.

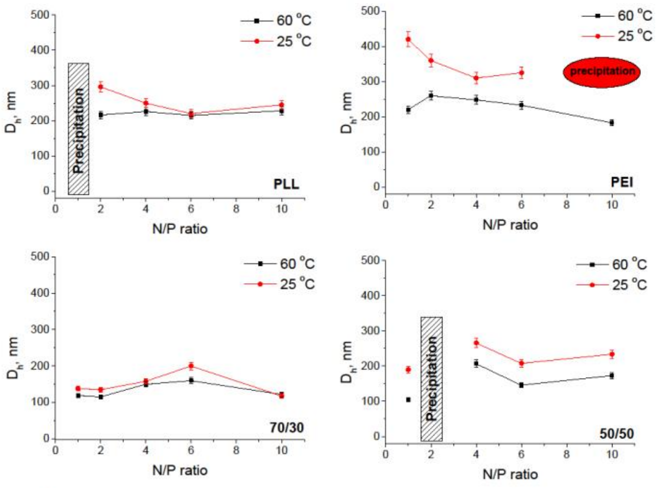
The molecular characteristics of the copolymers were as follows:
PNIPAm-PEG-PLL denoted as **PLL**, Mn=15 200 g/mol, cationic content 10 wt%;
PIPOX-PEI denoted as **PEI**, Mn=7 300 g/mol, cationic content 50 wt%.

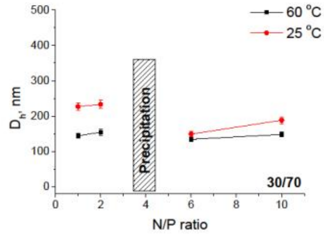
Mesoglobule composition	D_h^{60} nm	ζ potential ^{60} mV	1°/2° amine ratio
PLL	43	31.4	-
70:30	129	28.16	3:6
50:50	120	27.4	2:10
30:70	115	24.7	1:14
PEI	235	18.4	-

BINDING OF DNA

Polyplexes were prepared by drop-wise addition of appropriate amounts of water solution of DNA (salmon testes, 2000 bp) into a heated at 70 ºC aqueous dispersion of the mixed mesoglobules, under stirring. The DNA initial concentrations was 0.1 mg/ml. Polyplexes at N/P ratios in the range of 1 to 10 were prepared. The size and ζ potential of the systems were firstly determined at 60 ºC and then after cooling to 25 ºC.

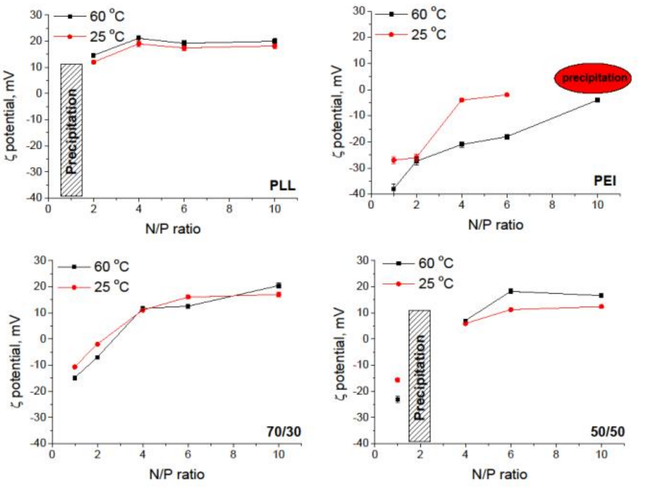
Size

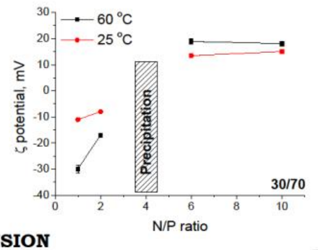




The size of polyplex particles formed from mixed mesoglobules was found to depend on their composition and temperature.

ζ potential





The ζ potential of polyplex particles formed from mixed mesoglobules was found to depend on their composition and the N/P ratio.

CONCLUSION

Positively charged mixed mesoglobules formed from PNIPAm-PEG-PLL and PIPOX-PEI copolymers were used for DNA condensation. They differed by composition as well as by primary to secondary amine ratio. Mesoglobules formed from pure copolymers were used as references. Polyplexes based on pure PLL precipitated at N/P=1. At N/P>1 the complexes were positively charged (ζ=18±3 mV) of size ca. 200 nm independently from temperature. Similar dimensions were determined for polyplexes formed from pure PEI at 60 ºC. In contrast, they were strongly negative independently from the N/P ratio and started to increase in size and even to precipitate upon cooling. The variations of D_h and ζ potential were completely different when mixed mesoglobules were used for complexation. Precipitation was detected at 50/50 and 30/70 compositions and the precipitation area shifted to higher N/P ratios with increasing PEI content. In general, the dimensions were smaller than those of the polyplexes prepared from the pure copolymer mesoglobules and without tending to increase upon cooling to 25°C. The ζ potential of all systems exhibited the typical sigmoidal curve pattern with values changing from negative to positive upon increasing N/P. In conclusion, important physicochemical parameters of the polyplex particles can be controlled by varying the composition of the mixed mesoglobules. Evaluation of their biological performance is the next goal of this study.

Acknowledgements: This work was supported by the Bulgarian Ministry of Education and Science (Grant D01-217/30.11.2018) under the National Research Programme "Innovative Low-Toxic Bioactive Systems for Precision Medicine (BioActiveMed)" approved by DCM # 658 / 14.09.2018

An approach for preparation of Spherical Nucleic Acids with liposomal cores

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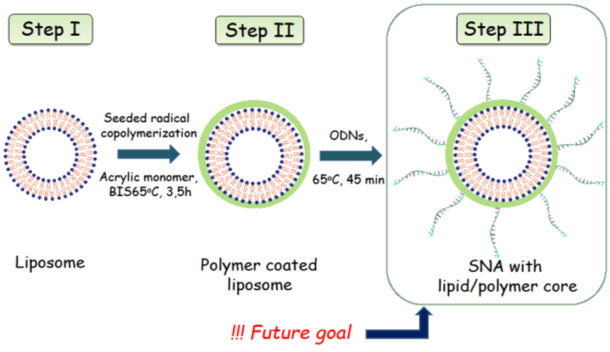
Introduction

Spherical nucleic acids (SNAs) are nanostructures composed of inorganic or organic cores to the surface of which highly oriented oligonucleotide strands are covalently attached thus forming a dense layer. The three-dimensional architecture of these structures gives rise to specific properties of SNAs that are different from those of their linear nucleic acid counterparts and are of great interest.

Herein, we employ a novel synthetic approach for preparation of SNAs with hybrid lipid/polymer cores. The approach involves three steps: (i) generation of a liposomal core, (ii) coating the core with a cross-linked polymeric shell, and (iii) grafting of the shell with oligonucleotide strands.



Step I

Step II

Step III

Seeded radical copolymerization

Acrylic monomer, BIS65°C, 3,5h

ODNs,

65°C, 45 min

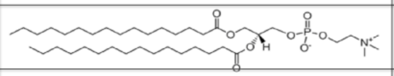
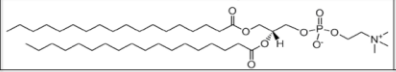
Liposome

Polymer coated liposome

SNA with lipid/polymer core

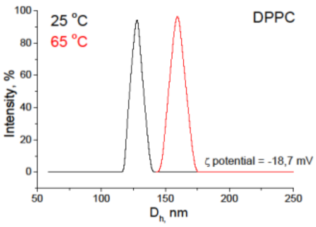
!!! Future goal

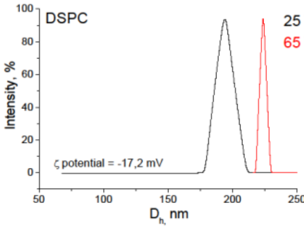
Preparation of liposomal cores

Lipid	Code	Structure	C atoms	T_m, °C
1,2-dipalmitoyl-sn-glycero-3-phosphocholine	DPPC		16	41
1,2-distearoyl-sn-glycero-3-phosphocholine	DSPC		18	55

Liposomes were prepared by freeze-thawing and extrusion of aqueous dispersions of the two lipids differing by T_m. Cholesterol was used as a membrane stabilizing agent.

The size and ζ potential of liposomes were determined by dynamic and electrophoretic light scattering at 25 and 65 °C. The size of the DPPC based liposomes was around 125 nm while that of DSPC was larger (ca. 190 nm). Increasing the temperature results in a slight increase of particles size. All liposomes were negatively charged.





Coating of liposomal cores

The coating of liposomes was achieved by seeded radical copolymerization of an acrylic monomer (*N*-isopropylacrylamide, NIPAM, or 2-Hydroxyethylmethacrylate, HEMA) and N,N-methylenbisacrylamide used as a cross-linking agent, initiated by 2,2'-azobis(2-methylpropionamidine) dihydrochloride. The polymer shell thickness was controlled by the initiator to monomer (I/M) molar ratio.

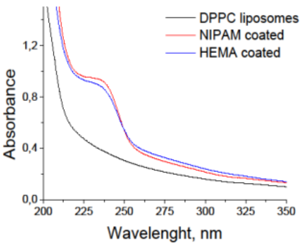
Indications for the successful coating of liposomes were the increase of particle size and the change of the initial ζ potential value. The formation of a polymer layer on the liposomal surface was detected spectrophotometrically by the appearance of characteristic absorption bands of NIPAM and HEMA at around 230 nm.

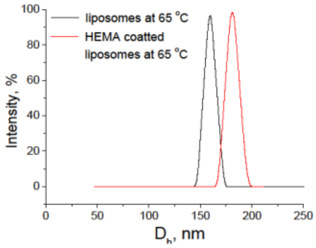
Liposomes	Coating	$D_h^{65\ °C}$ nm	$D_h^{25\ °C}$ nm	ζ potential $^{25\ °C}$ mV	Shell thickness, nm	I/M ratio
DPPC	NIPAM	229	157	-17.2	36.5	0.1
		266	165	-20.1	55	0.3
	HEMA	169	146	-21.0	7	0.1
		182	155	-19.1	13	0.3

Liposomes	Coating	$D_h^{65\ °C}$ nm	$D_h^{25\ °C}$ nm	ζ potential $^{25\ °C}$ mV	Shell thickness, nm	I/M ratio
DSPC	NIPAM	323	530	-2.4	67	0.1
		460	910	-2.1	135	0.3
	HEMA	262	298	-13.8	36.5	0.1
		274	221	-19.6	42.5	0.3

Conclusions

A new strategy for preparation of SNAs with hybrid lipid/polymer cores was proposed. The obtained liposomes were of small size, narrow size distribution and negative ζ potential. Polymer layers based on NIPAM or HEMA were successfully formed on the liposomal surface. The presence of polymer coating was proved by UV absorption, dynamic and electrophoretic light scattering analysis.





Future goals

- ✓ Grafting of the polymer shell with short oligonucleotide strands.
- ✓ Physicochemical characterization of the resulting structures.
- ✓ Biological evaluation of the novel SNAs with hybrid lipid/polymer cores.

Acknowledgement:

This work was funded by the National Science Fund of Bulgaria, Project № DN19-8.

Повърхностно присаждане на въглехидрати върху яйчена мембрана за получаване на структура тип „четка“. Потенциално приложение за филтърни материали.

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Въведение

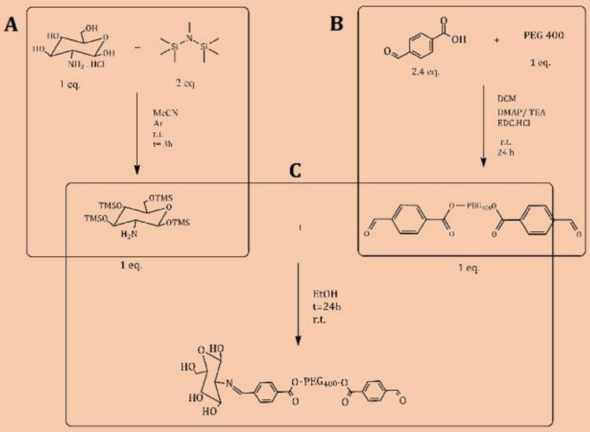
В природата има много примери за мембрани, които играят ролята на материали за филтруване, като например мембраната на яйчената черупка (ESM). ESM е физически стабилна, пореста, евтина (счита се за отпадък), и притежава както антибактериални функции, така и способността за задържане на органични молекули и метални йони. Съставът ѝ се състои от гликани и протеини, което я прави лесен за модификация материал.

Въглехидратите са природни вещества с важни функции в живите организми. Те се намират по повърхността на клетките и са отговорни за разпознавателните им свойства, т.е. свързват се селективно към протеини (например вируси). Доколкото ни е известно, тази характеристика на въглехидратите не е използвана до сега при разработване на филтърни материали.

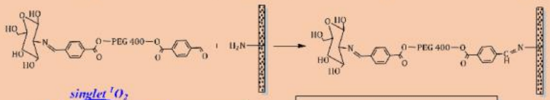
Настоящата работа представя една от стратегиите за модифициране на ESM, а именно чрез прикачване на алдехид-съдържащи захари към аминогрупите на мембраната за получаване на структура тип „четка“. Така модифицираната ESM ще бъде част от първия слой на филтърен материал (Фиг. 1).

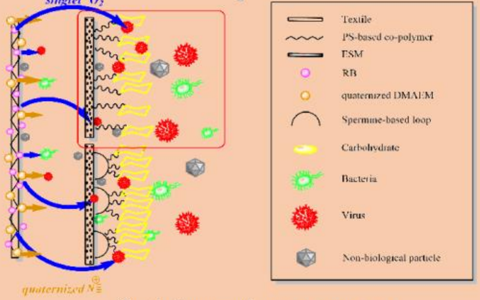
Процедура и Методи

- Отделяне на ESM от сурово яйце;
- Синтез на (2-амино-2-деокси-1,3,4,6-тетра-O-триметил силил-алфа-β-D-гликопираноза) (**A**);
- Синтез на ароматен диалдехид (**B**);
- Синтез на алдехид-съдържащо производно на въглехидрат (**C**);



- Модификация на ESM чрез реакция на повърхностните амино групи с алдехид-функционализирани въглехидрати;

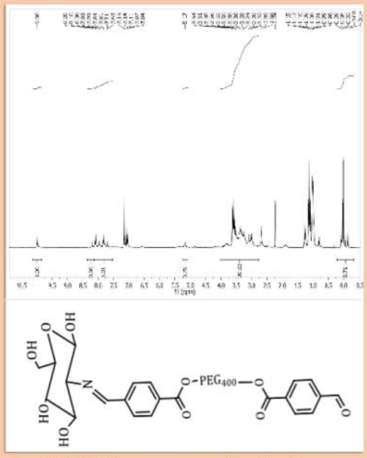




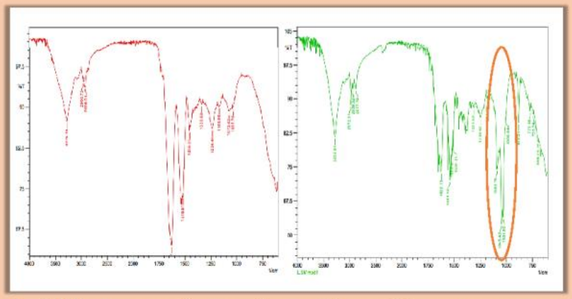
Фиг. 1: Двуслоен филтърен материал.

- Продуктите на реакции (A), (B), и (C) са охарактеризирани с ЯМР-спектроскопия (Bruker 250 MHz и 600 MHz), а модификацията на ESM е доказана чрез ИЧ-спектроскопия.

Резултати



Фиг. 2: ^{1}H ЯМР-спектър на алдехид-съдържащо производно на въглехидрат.



Фиг. 3: ИЧ-спектри на яйчена мембрана преди и след функционализиране с алдехидсъдържащ въглехидрат

Интензивните абсорбционни ивици, които се наблюдават в областта от 1100 до 1000 1/cm на ИЧ-спектъра на модифицираната мемебрана, доказват присаждането на веригите от ПЕГ със захарни остатъци.

Заключение

- За пръв път е модифицирана повърхността на яйчена мембрана (ESM) в структура тип „четка“ с въглехидрати с цел получаване на активен слой, чиято функция е да защитава и улавя частици от биологичен (био-разпознавателни свойства) и небиологичен произход.
- Предстоят тестове за биоразпознавателни свойства с протеин (Concanavalin A).

Благодарности

NATIONAL PROGRAMME „POST-DOCTORAL STUDENTS“ Funded by the Bulgarian Ministry of Education and Science (MES)

Нови поли(ε-капролактон)/полиглицидол линейни и звездовидни блокови съполимери чрез използване на „click“ химични реакции: синтез и охарактеризиране

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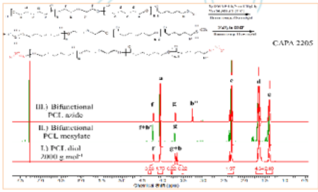
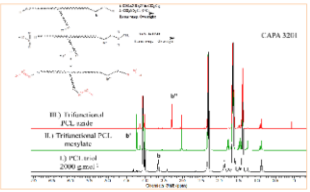
Въведение:

Полимерните наночастици продължават да привличат научен интерес, свързан както с фундаментални изследвания, така и с разнообразните възможности за техни приложения в различни области. Целта на настоящата работа е да се синтезират добре дефинирани, амфифилни, блокови съполимери с разнообразна архитектура (линейни и звездовидни), съставени от биопоносими и биоразградими сегменти. От особена важност, свързана с текущи изследвания, е синтезът на съполимерите да се извърши чрез високо-ефективни реакции на сдвояване – т. нар. *click реакции*. Бяха получени ди-, три- и тетраазидо функционални макроагенти на основата на поли(ε-капролактон) (ПКЛО) чрез реакционна процедура, включваща мезилиране на крайните хидроксилни групи и последваща реакция с NaN_3. Бяха синтезирани и макроагенти на основата на монохидроксил завършен поли(етоксиетил глицидилов етер) (ПЕЕГЕ), получени чрез анионна полимеризация с отваряне на пръстена и последващо фунционализиране на крайната хидроксилна в алкинова група. Чрез *азид-алкин click реакция*, проведена в присъствие на CuBr/PMDETA каталитичен комплекс, и последващо освобождаване на защитните етоксиетилови групи на ПЕЕГЕ бяха получени блокови съполимери на основата на ПКЛО и линеен полиглицидол с линейна и звездовидна (с три и четири рамена) архитектура. Молекулно-масовите характеристики и структурата на съполимерите бяха потвърдени чрез ГПХ, ИЧС и ЯМР и беше доказан техният състав.

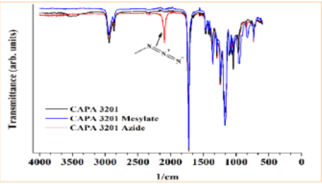
Етап 1. Получаване на азидотерминирани би-, три- и тетрафункционални поли(ε-капролактони)



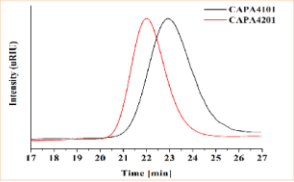
¹H ЯМР спектри на бифункционален ПКЛО-диол и съответващите мезилат и азид.



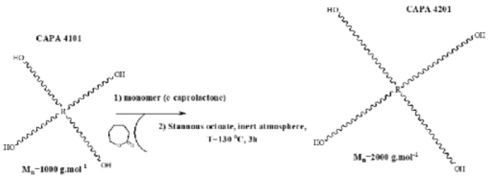
¹H ЯМР спектри на трифункционален ПКЛО-триол и съответващите мезилат и азид.



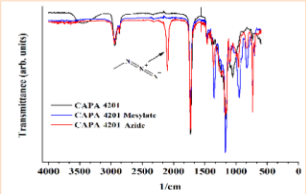
ИЧ спектри на трифункционален ПКЛО мезилат и азид.



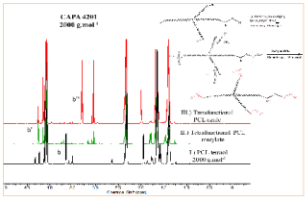
GPC на тетрафункционален поли(ε-капролактон) преди и след удължаването.



Удължаване на тетрафункционален PCL до молекулна маса 2000 в присъствие на калаен октоат.

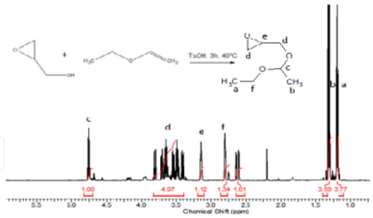


ИЧ спектри на тетрафункционален ПКЛО мезилат и азид.

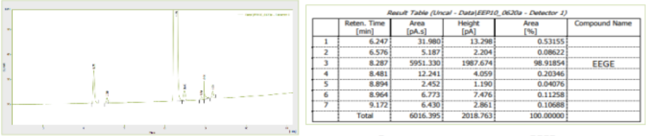


¹H ЯМР спектри на тетрафункционален ПКЛО мезилат и азид.

Етап 2. Получаване на етоксиетилглицидилов етер (ЕЕГЕ)



¹H ЯМР спектър на ЕЕГЕ.

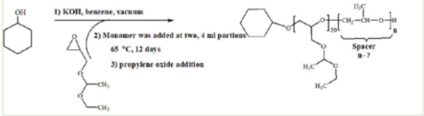


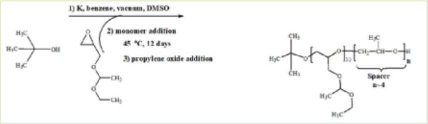
Result Table (Uncal - Data\EEP10_0620a - Detector 1)

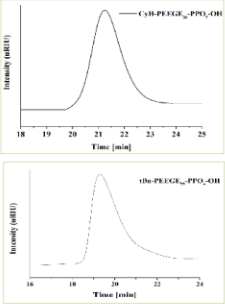
	Reten. Time [min]	Area [pA.s]	Height [pA]	Area [%]	Compound Name
1	6.247	31.980	13.298	0.53155	
2	6.576	5.187	2.204	0.08622	
3	8.287	5951.330	1987.674	98.91854	EEGE
4	8.481	12.241	4.059	0.20346	
5	8.894	2.452	1.190	0.04076	
6	8.964	6.773	7.476	0.11258	
7	9.172	6.430	2.861	0.10688	
	Total	6016.395	2018.763	100.00000	

Газова хроматограма на ЕЕГЕ.

Етап 3. Анйонна полимеризация на ЕЕГЕ.

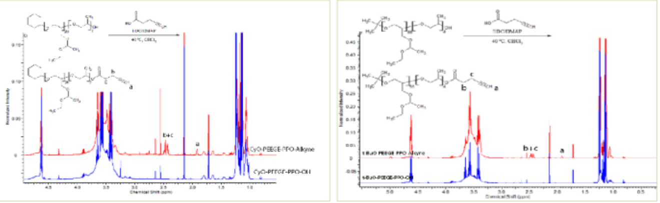






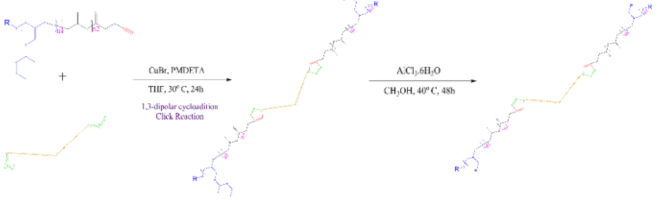
ГПХ на ПЕЕГЕ.

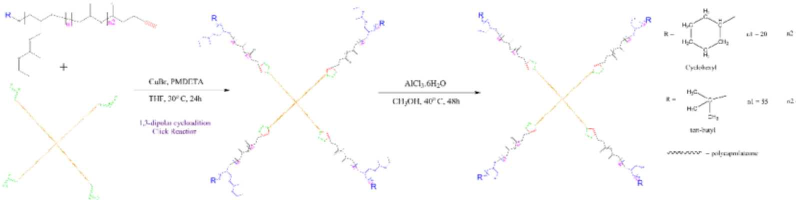
Етап 4. Естерифициране с 4-пентинова киселина.



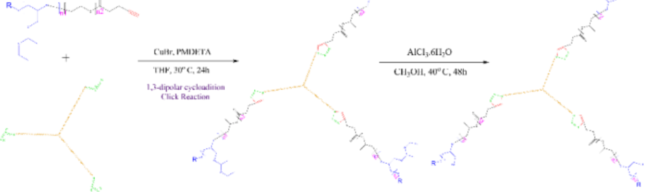
¹H ЯМР спектри на изходните и алкин-функционализираните ПЕЕГЕ.

Етап 5. Азид-алкин click реакции за получаване на ПКЛО-ПЕЕГЕ блок съполимери с линейна и звездовидна архитектура.





Етап 6. Хидролиза на защитните групи за получаване на ПКЛО-полиглицидол блок съполимери с линейна и звездовидна архитектура.



Код	M_n [g.mol⁻¹]	M_w/M_n
PCL2000-N_3	2 200	1.1
t-Bu-PEEGE$_{55}$-PPO$_4$-C≡CH	7 100	1.2
Съполимер	16 500	1.4

Литература:

1. Bakardzhiev, P.; Toncheva-Moncheva, N.; Mladenova, K.; Petrova, S.; Videv, P.; Moskova-Doumanova, V.; Topouzova-Hristova, T.; Doumanov, J.; Rangelov, S. Assembly of Amphiphilic Nucleic Acid–Polymer Conjugates into Complex Superaggregates: Preparation, Properties, and in vitro Performance. *Eur. Polym. J.* 2020, 131, 109692. https://doi.org/10.1016/j.eurpolymj.2020.109692

2. Toncheva-Moncheva, N.; Bakardzhiev, P.; Rangelov, S.; Trzebicka, B.; Forys, A.; Petrov, P. Linear Amphiphilic Polyglycidol/Poly(ε-caprolactone) Block Copolymers Prepared via "Click" Chemistry-based Concept. *Macromolecules* 2019, 52 (9), 3435-3477. DOI: 10.1021/acs.macromol.9b00366

Обобщение

1. Успешно са получени *азидотерминирани* ди-, три- и тетрафункционални поли(ε-капролактони) с молекулна маса 2000 g/mol.
2. Синтезиран е етоксиетилглицидилов етер (ЕЕГЕ) с чистота 98,9%.
3. Проведени са две анйонни полимеризации с отваряне на пръстен на ЕЕГЕ, с два различни инициатора. Получени са два хомополимера ПЕЕГЕ с молекулни маси 3000 и 8000 g/mol с ниска дисперсност.
4. Получените ПЕЕГЕ успешно са *функционализирани чрез естерифициране с 4-пентинова киселина.*
5. Чрез *азид-алкин click реакции* са получени ПКЛО-ПЕЕГЕ блок съполимери с линейна и звездовидна архитектура.
6. След *хидролиза* на защитните етоксиетилови групи са получени ПКЛО-полиглицидол блок съполимери с линейна и звездовидна архитектура.
7. **Предстоят** изследвания за *способността на съполимерите да самоасоциират и съ-асоциират* с липиди или други молекули, образуващи немицеларни структури, с цел проучване на потенциала им като *наноносители на биологични (макро)молекули и биологично-активни вещества.*

Благодарности: **Настоящото изследване е проведено с подкрепата на Фонд Научни изследвания на МОН чрез проект КП-06-Н23/7 от 18.12.2018.**

Dual drug loaded mixed micelles for enhanced cancer therapy

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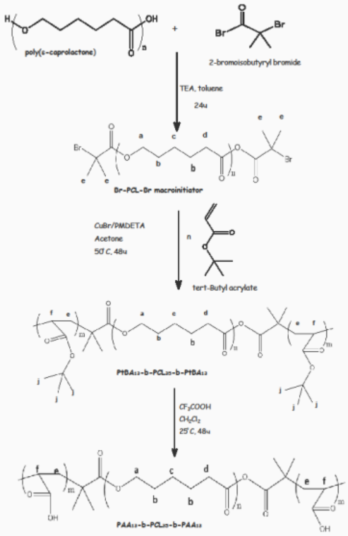
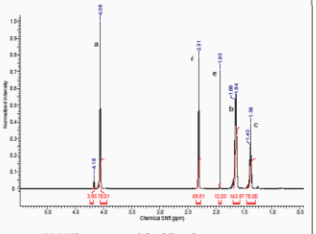
Introduction

Recently drug delivery systems based on block copolymer nanoparticles have focused much attention for controlled delivery of cancer therapeutics. Multifunctional nanosystems have been used as carriers of two or more anticancer drugs with different pharmacological mechanisms for combination therapy, which aims at achieving synergistic effect in cancer curing and overcoming the increasingly common problem of drug resistance. Amphiphilic block copolymers frequently self-assemble in aqueous media into spherical core-shell micelles. Controlled polymerization techniques are preferred for the synthesis of well-defined block copolymers enabling fine tuning of the macromolecular structure, composition, and functionality. All these factors play important role considering the preparation of polymeric aggregates for applications in the biomedical areas.

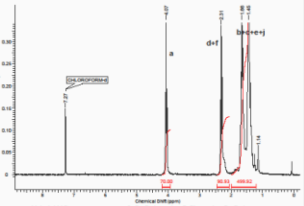
Aim: This work aims at developing functional mixed nano-sized micellar carriers of two bioactive substances, doxorubicin (DOX) and caffeic acid phenethyl ester (CAPE). Nanocarriers were prepared by co-assembly of two well-defined amphiphilic triblock copolymers, poly(ethylene oxide)-block-poly(ε-caprolactone)-poly(ethylene oxide) (PEO-b-PCL-b-PEO) and poly(acrylic acid)-block-poly(ε-caprolactone)-block-poly(acrylic acid) (PAA-b-PCL-b-PAA).

Synthesis of PAA_{13}-b-PCL_{35}-b-PAA_{13} triblock copolymer via Atom transter radical polymerization on tBA and hydrolysis

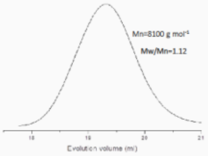




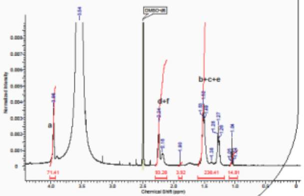
^{1}H-NMR spectrum of Br-PCL_{35}-Br macroinitiator



^{1}H-NMR spectrum of $PtBA_{13}$-b-PCL_{35}-b-$PtBA_{13}$ triblock copolymer

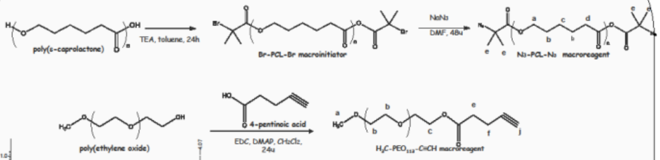


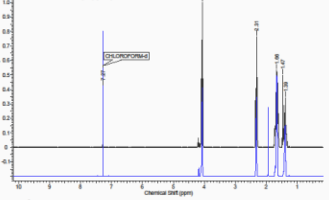
GPC chromatograms of $PtBA_{13}$-b-PCL_{35}-b-$PtBA_{13}$ triblock copolymers



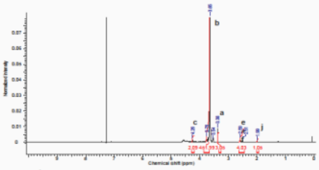
^{1}H-NMR spectrum of PAA_{13}-b-PCL_{35}-b-PAA_{13} triblock copolymer

Synthesis of PEO_{113}-b-PCL_{35}-b-PEO_{113} triblock copolymer by "Click" reaction

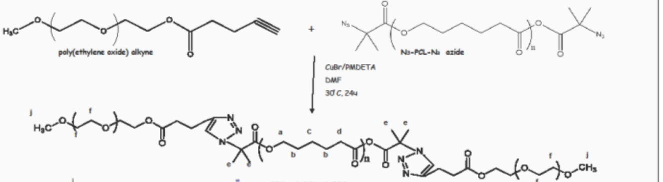


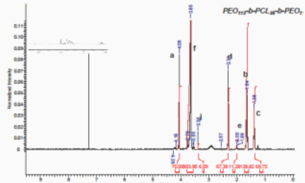


^{1}H-NMR spectrum of Br-PCL-Br precursor(blue) and N_3-PCL-N_3 macroreagent (black)

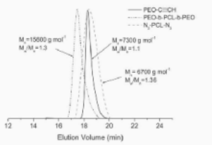


^{1}H-NMR spectrum of HC≡C-PEO_{113}-C≡CH macroreagent



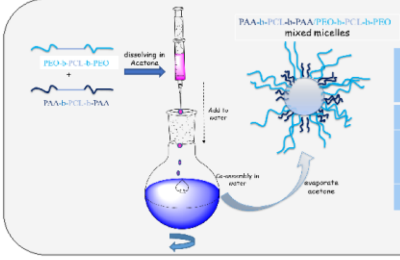


^{1}H-NMR spectrum of of PEO_{113}-b-PCL_{35}-b-PEO_{113} triblock copolymer



GPC chromatograms of PEO_{113}-b-PCL_{35}-b-PEO_{113} triblock copolymers and both precursors

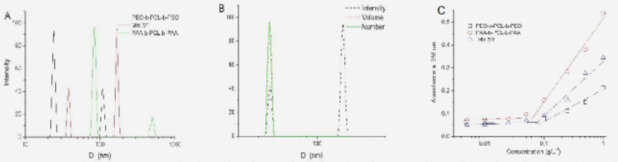
Preparation of mixed micelles



Determining of the particles size, size distribution and ζ-potentional by Dynamic Light Scattering

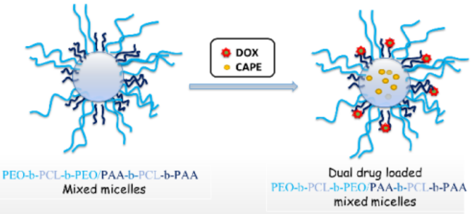
Copolymers	D_h (nm)	ζ potential (mV)	CMC (g L⁻¹)
PEO_{113}-b-PCL_{35}-b-PEO_{113}	26	-0,6	0.090
PEO_{113}-b-PCL_{35}-b-PEO_{113} / PAA_{13}-b-PCL_{35}-b-PAA_{13} (mol. ratio 3:1)	38	-22	0.078
PAA_{13}-b-PCL_{35}-b-PAA_{13}	86	-33	0.063

Determination of the critical micellar concentration of single- and mixed copolymer micelles.



Comparison of: (A) intensity-weighted size distribution plots of single-polymer micelles and mixed micelles (3:1 mol ratio), and (B) size distribution of the mixed micelles plotted by intensity, volume, and number, (C) CMC of copolymer micelles

Dual drug loading into mixed micelles



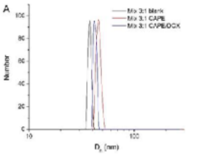
PEO-b-PCL-b-PEO/PAA-b-PCL-b-PAA
Mixed micelles

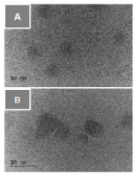
Dual drug loaded
PEO-b-PCL-b-PEO/PAA-b-PCL-b-PAA
mixed micelles

CAPE was entrapped into the PCL core via hydrophobic interactions.

DOX was loaded in the middle layer through complexation .

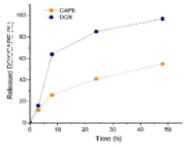
Hydrodynamic diameter plots of blank and drug loaded mixed micelles



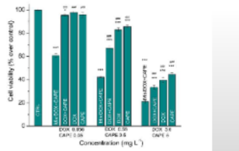


Transmission electron micrographs of: (A) blank and (B) dual drug loaded mixed micelles

Drug release and cytotoxicity



Simultaneous in-vitro release of DOX and CAPE in a phosphate buffer (pH=7.4).



Viability of mouse T-lymphoma L5178Y MDR1 cell line after 72 h treatment with DOX/CAPE loaded micelles, combination of free DOX+CAPE, free DOX and free CAPE.

Conclusions:

Two well-defined amphiphilic block copolymers were successfully synthesized. Amphiphilic PEO-b-PCL-b-PEO triblock copolymer was obtained by copper mediated "click" coupling reaction of preliminary modified PEO-monomethyl ether and PCL-diol. Amphiphilic PAA-b-PCL-b-PAA triblock copolymer was synthesized via ATRP and subsequent hydrolysis. NMR and GPC results revealed that the two reactions were well-controlled. Functional micellar nanocarriers for co-delivery of doxorubicin and caffeic acid phenethyl ester were successfully developed by co-assembly of PEO_{113}-b-PCL_{35}-b-PEO_{113} and PAA_{13}-b-PCL_{35}-b-PAA_{13} in water. The proper design of copolymer composition, macromolecular characteristics and functionality afforded the formation of nano-sized carriers comprising a PCL core, a middle PAA/PEO layer and a protecting PEO outer layer. CAPE was entrapped into the PCL core via hydrophobic interactions, while DOX molecules were loaded in the middle layer through complexation between the amino and carboxylic groups of DOX and PAA, respectively. The dual drug loaded micellar carriers exhibited superior colloid stability and sustained drug release profile. The developed system has good potential for effective antitumor therapy and for reducing the negative adverse effects.

Acknowledgements: This study was support by the Bulgarian National Science Fund (Grant DN09/1 - 2016).

Постер 11

Nanoparticle diffusion in polymer melts: Molecular dynamics simulations and mode-coupling theory

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[4]Leibniz Institut für Polymerforschung Dresden, Hohe Strasse 6, D-01 069 Dresden, Germany

БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ
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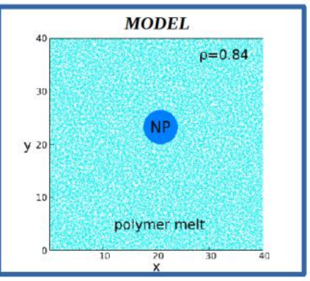
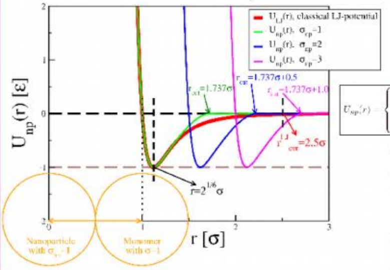
INTRODUCTION: Nanoparticle diffusion in polymer melts is studied by combination of Molecular Dynamics (MD) simulations and Mode-Coupling Theory (MCT). In accord with earlier experimental, simulation, and theoretical studies, we find that the Stokes-Einstein (SE) hydrodynamic relation $D_n \sim 1/R_n$ holds when the nanoparticle radius R_n is greater than the polymer gyration radius R_g while in the opposite regime the measured nanoparticle diffusion coefficient D_n exceeds the SE value by as much as an order of magnitude. The MCT values of D_n are found to be consistently higher than the MD simulation values. The observed discrepancy is attributed to approximations involved in constructing the microscopic friction as well as to the approximate forms for dynamic structure factors used in MCT. In a thorough test of underlying MCT assumptions and approximations, various structural and dynamical quantities required as input for MCT are obtained directly from MD simulations. We present improved MCT approach, which involves splitting the microscopic time-dependent friction into two terms: binary (originating from short-time dynamics) and collective (due to long-time dynamics). Using MD data as input in MCT, we demonstrate that the total friction is largely dominated by its binary short-time term, which, if neglected, leads to severe overestimation of D_n. As a result, the revised version of MCT, in agreement with the present MD data, predicts $1/R_n^2$ scaling of the probe diffusion coefficient in non-hydrodynamic regime when $R_n < R_g$. If the total friction is dominated by the collective long-time component, one would observe $1/R_n^3$ scaling of D_n in accordance with previous studies.

MODEL



POTENTIALS: 1) Potential between *nanoparticle* and monomers



Nanoparticle radius $R_n = 0.5 \div 5$
Polymer chain length $N = 10 \div 240$
Polymer gyration radius $R_g \approx 1.5 \div 8$

$$U_{np}(r) = \begin{cases} 4\epsilon_{np}\left[\left(\frac{\sigma}{r-R_{EV}}\right)^{12} - \left(\frac{\sigma}{r-R_{EV}}\right)^{6}\right], & \text{if} \quad R_{EV} < r < r_s + R_{EV} \\ a(r-R_{EV}-r_c)^2 + b(r-R_{EV}-r_c)^3, & \text{if} \quad r_s + R_{EV} \le r < r_c + R_{EV} \\ 0, & \text{if} \quad r_c + R_{EV} \le r. \end{cases}$$

$R_{EV} = R_n - \sigma/2$ $\qquad a = -(24192/3211)(\epsilon_{np}/r_s^2)$

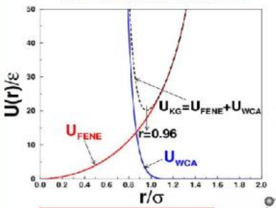
$r_s = (26/7)^{1/6}\sigma$ $\qquad b = -(387072/61009)(\epsilon_{np}/r_s^3)$

$r_c = (67/48)r_s$

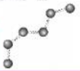
$\epsilon_{np} = \epsilon = 1$, $M_n = m = 1$, and $\sigma = 1$

F. Bresme and N. Quirke, Phys. Rev. Lett. 80, 3791 (1998)
B. L. Holian and D. J. Evans, J. Chem. Phys. 78, 5147 (1983)

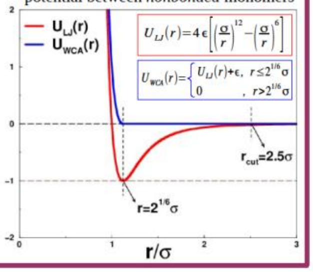
2) Kremer-Grest (FENE+WCA) potential between *bonded* monomers



$U_{FENE}(l) = -0.5 K r_0^2 \ln\left[1-(r/r_0)^2\right]$
$r_0 = 1.5\sigma, \quad k = 30\epsilon/\sigma^2$



3) Weeks-Chandler-Andersen (WCA) potential between *nonbonded* monomers



$$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$U_{WCA}(r) = \begin{cases} U_{LJ}(r)+\epsilon, & r \le 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases}$$

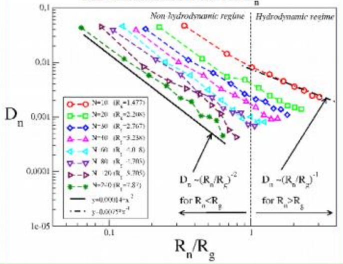
Nanoparticle diffusion coefficient D_n

$$D_n = D_{hydro} + D_{micro}$$

$R_n > R_g$: $\quad D_{hydro} = \frac{k_B T}{6\pi\eta R_n}$

$R_n < R_g$: $\quad D_{micro} = \frac{k_B T}{M_n \zeta_{micro}}$

MD simulation results for D_n



Mode-Coupling Theory (MCT)

$$\zeta_{micro} = \frac{k_B T \rho}{6\pi^2 m N}\int_0^\infty dt \int_0^\infty dk k^4 c_{np}(k)^2 S_{pp}(k) F(k,t) F_s(k,t)$$

$$F(k,t=0) = F_s(k,t=0) = 1$$

$$F_s(k,t) = \exp[-k^2 D_n t]$$

$$F(k,t) = \exp\left[-\frac{k^2 D_p t}{S_{pp}(k)}\right]$$

$$\zeta_{micro}(0) = \frac{k_B T \rho}{6\pi^2 m N}\int_0^\infty dk k^4 c_{np}(k)^2 S_{pp}(k)$$

$$\zeta_b(0) = \frac{4\pi\rho}{3M_n}\int_0^\infty dr r^2 g_{np}(r) \nabla^2 U_{np}(r)$$

U. Balucani and M. Zoppi, Dynamics of the Liquid State (Clarendon: Oxford 1994)

Molecular Dynamics (MD) measurements:

$$D_n = \frac{1}{2d}\lim_{t\to\infty}\frac{\langle\Delta r^2(t)\rangle}{t} \qquad S(k) = 1 + 4\pi\rho\int_0^\infty dr r^2 \left(\frac{\sin(kr)}{kr}\right)[g(r)-1]$$

$$F(k,t) = \left[\frac{1}{N_{tot}}\sum_{i=1}^{N_{tot}}\sum_{j=1}^{N_{tot}}\left(\frac{\sin(kr_{ij}(t))}{kr_{ij}(t)}\right)\Delta_{ij}(R,t) - \frac{4\pi\rho}{k^2}\left(\frac{1}{k}\sin(kR) - R\cos(kR)\right)\right] \Big/ F(k,0)$$

$$\Delta_{ij}(R,t) = \begin{cases} 1, & \text{if } r_{ij}(t) \le R \\ 0, & \text{if } r_{ij}(t) > R \end{cases}$$

J. J. Salacuse and P. A. Egelstaff., Phys. Rev. E 64, 051201 (2001)
Neil E. Moe and M. D. Ediger, Phys. Rev. E 59, 623 (1999)

Revised Mode-Coupling Theory

$$\zeta_{micro} = \int_0^\infty dt \zeta_{short}(t) + \int_0^\infty dt \zeta_{long}(t)$$

$$\zeta_{long}(t) = \frac{k_B T \rho}{6\pi^2 m N}\int_0^\infty dk k^4 c_{np}(k)^2 F(k,t)[F_s(k,t) - F_{s0}(k,t)]$$

$$F_s(k,t) = \exp\left[\frac{-k_B T k^2}{M_n \zeta}\left(t + \frac{1}{\zeta}(e^{-t\zeta} - 1)\right)\right]$$

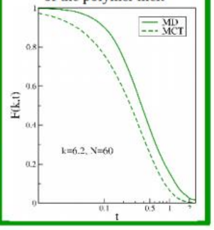
$$F_{s0}(k,t) = \exp\left[-\frac{k_B T k^2 t^2}{2M_n}\right]$$

$$\zeta_{short}(t) = \zeta_b(0)\exp(-t^2/\tau^2)$$

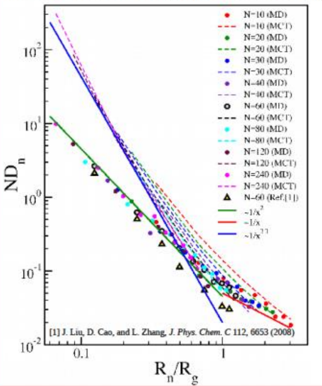
$$D_n = \frac{k_B T}{6\pi\eta R_n} + \frac{k_B T}{M_n(\zeta_{short} + \zeta_{long})}$$

H. Popova, S. Egorov, A. Milchev, *J. Chem. Phys.* **152**, 234902 (2020)

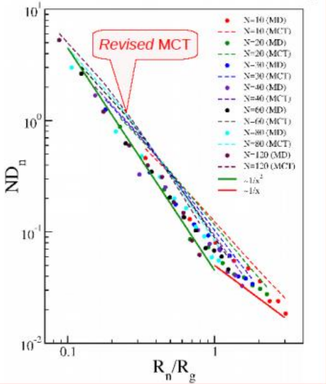
Intermediate scattering function of the polymer melt



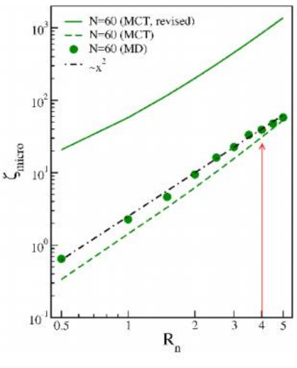
MD simulation and MCT theoretical results for nanoparticle diffusion coefficient D_n as a function of the nanoparticle radius R_n scaled by the polymer gyration radius R_g

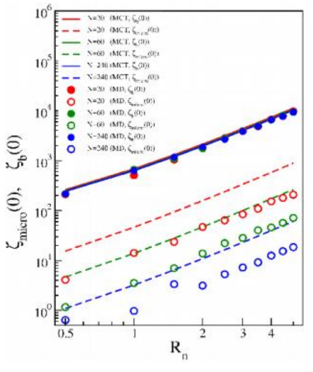


[1] J. Liu, D. Cao, and L. Zhang, *J. Phys. Chem.* C 112, 6653 (2008)



MD simulation and MCT theoretical results for total microscopic friction ζ_{micro} and microscopic time-dependent friction at time t=0 vs nanoparticle radius R_n





CONCLUSIONS

- We present an extensive comparison between MD simulation and MCT theoretical results for the diffusion coefficient of a nanoparticle in a polymer melt of flexible chains.
- We present an improved MCT approach which involves splitting the microscopic time-dependent friction into two terms: short-time binary term and long-time collective term. The key finding is that the microscopic friction is largely dominated by the short-time binary contribution and the neglect of the latter leads to severe overestimation of the nanoparticle diffusion coefficient.
- The revised version of MCT, in agreement with the present MD data, predicts the size-dependent scaling of the nanoparticle diffusion coefficient following $1/R_n^2$ behavior when the nanoparticle radius R_n is smaller than the gyration radius R_g of the polymer chains in the melt, while in the opposite regime,when $R_n > R_g$, the expected Stokes-Einstein $1/R_n$ behavior is observed.

LOADING OF CIPROFLOXACIN INTO POLYMERIC MICELLES OF DIFFERENT COMPOSITION

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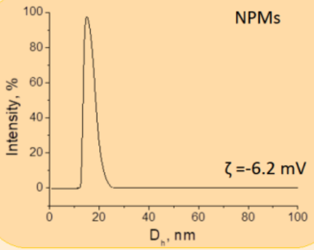
Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl.103-A, Sofia 1113

INTRODUCTION

Ciprofloxacin (CF) is a wide spectrum antibiotic approved by FDA against various bacterial infections. The effective antimicrobial therapy, however, depends on the CF solubility and its efficient delivery to the target site of infection. Polymeric micelles (PMs) have been extensively studied as drug delivery carriers. The micellar hydrophobic core ensures the solubilization of water insoluble drugs while the hydrophilic shell improves their biocompatibility, stability etc.

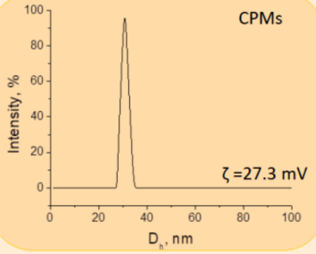
In this work the loading of CF into polymeric micelles of different composition was investigated. Non ionic polymer micelles (NPMs) formed from a triblock copolymer based on poly(ethylene oxide) and poly(propylene oxide), known as Pluronic F127, as well as cationic polymer micelles (CPMs) based on a poly(2-(dimethylamino)ethyl methacrylate)-b-poly(ε-caprolactone)-b-poly(2-(dimethylamino)ethyl methacrylate) triblock copolymer were used. The two systems were characterized by dynamic and electrophoretic light scattering. Encapsulation efficiency (EE) and drug loading content (DLC) were determined spectrophotometrically.

FORMATION OF POLYMER MICELLES



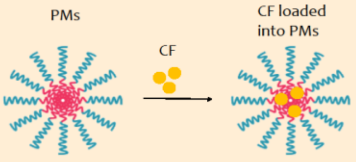
NPMs were formed in aqueous media under sonication at 60 °C, and polymer concentration of 1 mg/ml.

CPMs were prepared by dropwise addition of copolymer, dissolved in methanol to deionized water followed by evaporation of the organic solvent giving a final concentration of 1 mg/ml.



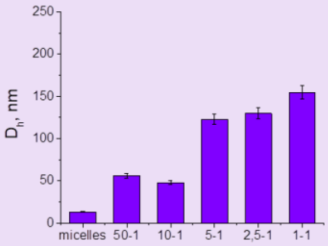
LOADING OF CIPROFLOXACIN

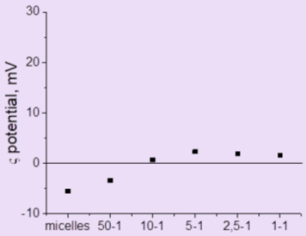
Loading of CF was performed by adding appropriate amount of drug powder to the micellar dispersion in order to obtain polymer to drug weight ratio in the rage of 1/1 to 50/1. The mixtures were first sonicated for 1 h at 60 °C for alleviating drug solubilisation and then filtered. The filters were rinsed with ethanol and the filter fractions were quantified spectrophotometrically in order to determine EE and DLC. The size and ζ potential of micelles loaded with CF were determined as well.

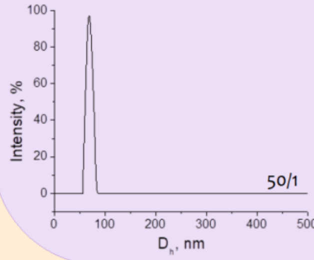


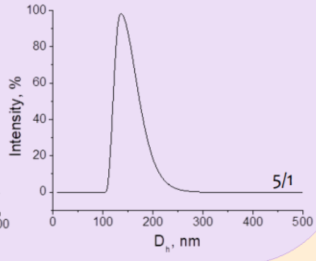
NPMs

Sample	EE %	DLC %
50-1	96.4	1.9
10-1	83.4	10.0
5-1	73.1	15.3
2,5-1	30.2	13.1
1-1	41.0	41.0



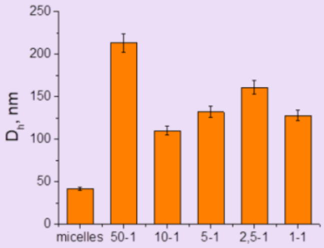


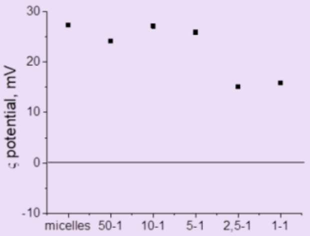


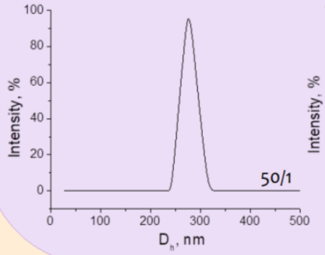


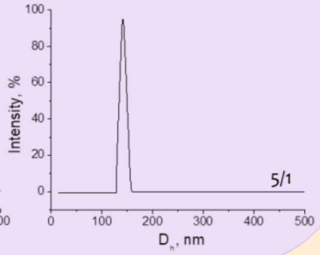
CPMs

Sample	EE %	DLC %
50-1	90.9	2.0
10-1	87.5	9.6
5-1	89.9	19.8
2,5-1	94.5	37.8
1-1	61.0	61.0









CONCLUSIONS

PMs of two different compositions were formed from poly(ethylene oxide)-b-poly(propylene oxide)-poly(ethylene oxide) and poly(2-(dimethylamino)ethyl methacrylate)-b-poly(ε-caprolactone)-b-poly(2-(dimethylamino)ethyl methacrylate) triblock copolymers, respevtively. The micelles possessed small size (D_h from 18-32 nm) and narrow size distribution. ζ-potential of NPMs were close to zero due to the presence of PEO hydrophilic shell, while the cationic PDMAEMA chains provoked strong positive value (ca. 27 mV) for CPMs. Both systems were effectively loaded with CF as the determined EE was in the range of 40-96 %. The DLC as well as the size of the micelles were found to increase with the CF concentration. The ζ-potential of NPMs was independent from the CF concentration. In contrast, for CPMs, the value started to decrease with increasing the CF amount. This could be due to the partial electrostatic interaction between PDMAEMA and the drug which is with negative potential at neutral pH. The developed micellar systems are considered promising candidates for treatment of bacterial infections.

Постер 13

Хибридни хидрогелове на поли(акрилова киселина-съ-акриламид) и магнетит

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Лаборатория по структура и свойства на полимерите, Факултет по химия и фармация, СУ „Св. Климент Охридски“

Въведение

Полимерните хидрогелове представляват ефективна матрица за получаването на метални частици с дефиниран състав и размер. Хибридните хидрогелове предоставят широк набор от възможности за приложение в различни направления напр. антибактериални покрития, катализатори и др.

Цел на изследването

► Разработване на хибридни хидрогелове на поли(акрилова киселина-съ-акриламид) и магнетит като нов интелигентен материал;

Задачи

► Синтез на съполимерни хидрогелове на поли(акрилова киселина) и полиакриламид с *in situ формирани магнетитни частици.*

► Изследване свойствата на получените хибридни хидрогелове

Синтез на хидрогелове без и с in situ формиран магнетит

стъкло

Акрилова киселина, акриламид,
Калиев персулфат (0.3 mol%),
N,N'-метилен-бис-акриламид (2 mol%

стъкло

60°C, 45min

Измиване и сушене

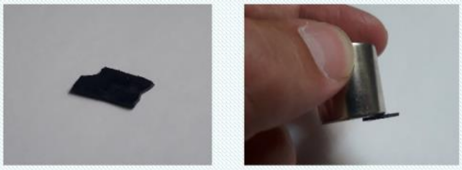
Набъбване в Fe^{2+}/Fe^{3+}

Набъбване в NaOH

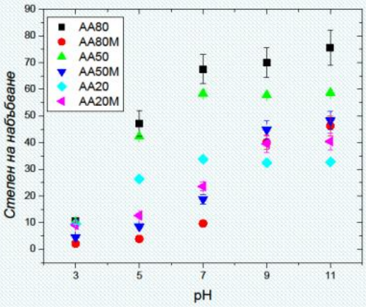
Измиване и сушене

Таблица 1. Състав на получените хидрогелове

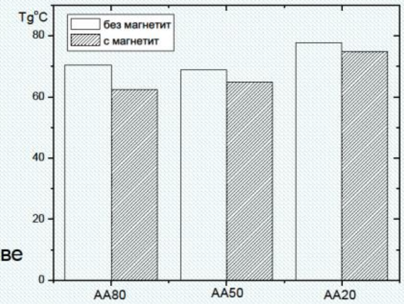
Проба	АК (мол%)	ААМ (мол%)	Магнетит
АА80	80	20	-
АА50	50	50	-
АА20	20	80	-
АА80М	80	20	+
АА50М	50	50	+
АА20М	20	80	+



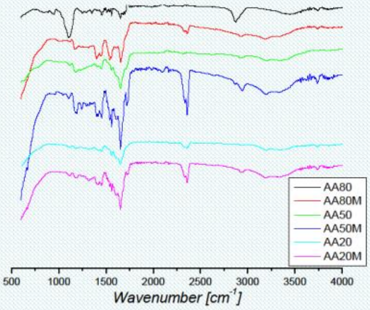
Фигура 1. Външен вид и демонстрация на магнитните свойства на получените хидрогелове АА50М (в сухо състояние).



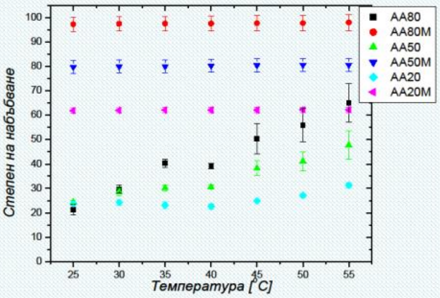
Фигура 2. pH чувствителност на хидрогеловете с и без формиран *in situ* магнетит



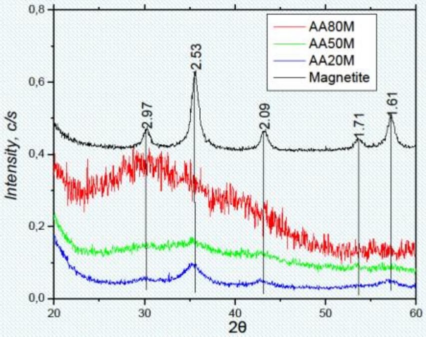
Фигура 4. Термични свойства на получените хидрогелове с и без формиран *in situ* магнетит



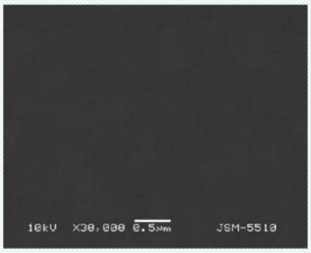
Фигура 5. ИЧ спектри на получените хидрогелове с и без формиран *in situ* магнетит



Фигура 3. Температурна чувствителност на хидрогеловете с и без формиран *in situ* магнетит



Фигура 5. Дифрактограми на получените хидрогелове с формиран *in situ* магнетит



Фигура 6. СЕМ изображение на проба АА50М

Заключение

► Успешно са синтезирани хидрогелове на поли(АК-съ-ААМ) с in situ формирани магнетитни частици;

► Получените хибридни хидрогелове проявяват pH чувствителност;

► Липсата на температурна чувствителност у хибридните хидрогелове се дължи на разрушаване на водородните връзки между страничните групи на ПАК и ПААМ (потвърдени с данните от ИЧ и ДСК).

► Съотношението ПАК/ПААМ повлиявавърху кристалността на формирания *in situ* магнетит (данни от ШЪРР).

Благодарности: *Това изследване е проведено с финансовата подкрепа на Фонд „Научни изследвания“ по проект* ***ДМ19/4.***

Нанокомпозитни катализатори от Ni, Co и Mn за алкална електролиза

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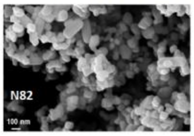
Синтезирани са катализаторите NiMn, CoMn, NiCoMn, Co30, Ni40 върху безвъглероден носител по зол-гел метод, като съдържанието на метал в тях е 40 т.% и 30т.%. Използвани са методите SEM и XRD за изследване на морфологията, химичната структура и фазите на катализаторите. За изследване влиянието на съставите върху каталитичната активност на катализаторите са използвани електрохимични тестове- циклична волтаметрия, поляризационни криви и потенциостатични криви. Катализаторите са тествани в алкална среда 25% KOH и полимерна анионпроводяща електролитна мембрана за реакциите на отделяне на водород и кислород.

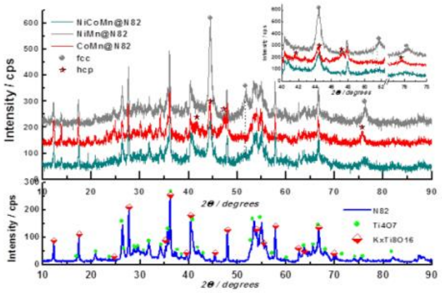
Зол-гел метод:

- ✓ Отлагане на Ni, Co и Mn като наночастици върху каталитичен носител MPT (Ti-dynamics Co.) N82
- ✓ Ацетилацетонатни прекурсори (M $((C_5H_7O_2)_n)_m$, (M = Ni, Co, Mn), (Alfa Aesar).
- ✓ Хомогенизиране на прекурсорите и носителя и изпичане при специална програма с плавно увеличение на температурата в редукционна атмосфера от H_2 при 240^0C

Каталитичен носител N82

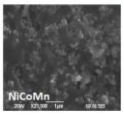
- ✓ Виоска електрична проводимост
- ✓ Корозионна устойчивост
- ✓ Две кристални фази:
  Магнели фази титан (Ti_4O_7)
  Холандит $KxTi_8O_{16}$ (1<x<1.2)
- ✓ Равномерно разпределение на частиците
- ✓ Размер на частиците 100-150 nm
- ✓ Повърхностна площ 45-50 $m^2.g^{-1}$

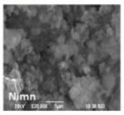


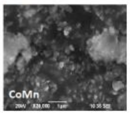


Катализатори

- ✓ NiMn/N82 - Ni-fcc (Ni-кубична сингония)
- ✓ CoMn/N82 - Co-hcp (Co-хексагонална сингония) и Co-fcc.
- ✓ NiCoMn/N82 - fcc фаза, NiCo твърд разтвор.
- ✓ Mn присъства под формата на оксид или шпинел
- ✓ Размер на кристалитите 14-40 nm



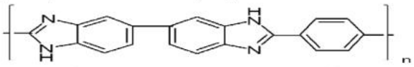




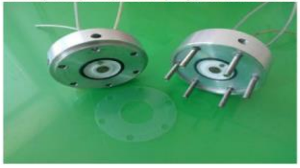
Membrane	RH 10%	RH 30%	RH 50%	RH 80%	RH 100%
p-PBI/KOH	298	600	842	1030	1140
p-PBI/MMT/KOH	235	610	1070	1320	1420

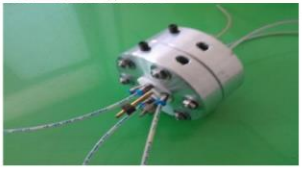
Анионна проводимост ($mS.cm^{-1}$) на p-PBI мембрани при 110 ° C и различна RH, p-PBI // KOH: 15.3 wt. % p-PBI, 84.7 wt. % Разтвор на електролит на KOH, p-PBI / 50% MMT / KOH: 5.5 wt. % p-PBI, 2,25 wt. % MMT, 92.25 тегл.% Разтвор на електролит на KOH. За 50% воден разтвор на KOH е измерена анионна проводимост при 100 °C от около 1400 $mS.cm^{-1}$.

H. Penchev, G. Borisov, E. Petkucheva, I. Radev, E. Slavcheva ,Highly KOH doped para-polybenzimidazole anion exchange membrane and its performance in Pt/$TinO_{2n-1}$ catalyzed water electrolysis cell, Materials Letters 221 (2018) 28-130

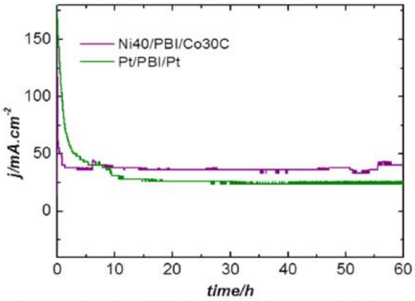


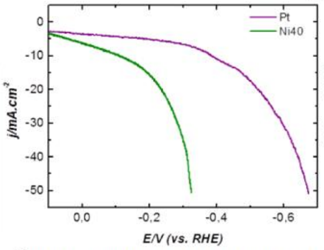
Електролизна клетка с 4 херметически изолирани камери, работеща с анионпроводяща мембрана (AEM), температурен диапазон на работа – от 25^0C до 160°C

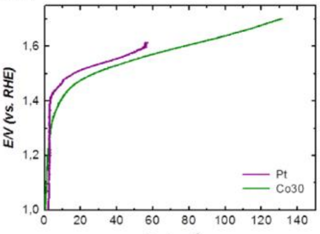




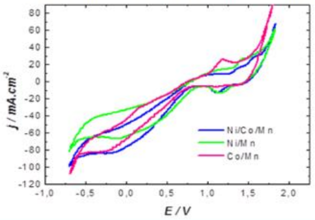
Потенциостатични криви,E =2 V, Мембранен електроден пакет (MEA) с Ni40 катод и Co30 анод



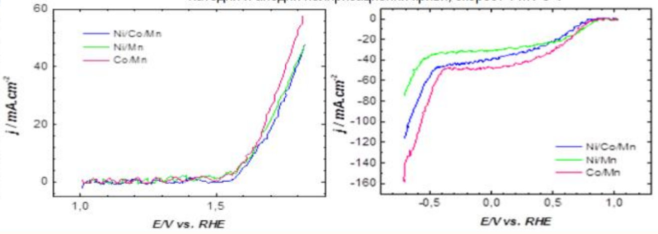




Циклична волтамограма, скорост 100 mV.s^{-1}



Катодни и анодни поляризационни криви, скорост 1 mV s^{-1}.



- ✓ Каталитичният носител N82 е подходящ и устойчив материал за приложение при водна електролиза и при електролиза с полимерна анионпроводяща мембрана (AEM)
- ✓ Изследваните композитни катализатори от неблагородни метали демонстрират висока ефективност спрямо реакциите на отделяне на водород и кислород, съчетано с корозионна устойчивост.
- ✓ MEA с вграден Ni / MPT катод и Co / MPT анод показват по-добри показатели на MEA с Pt / MPT електроди.
- ✓ Отчетената плътност на тока за за MEA с неблагороден метал, диспергиран върху интерактивен оксиден носител N82 е 36-38 mA .cm^{-2} . Тази стойност е 1,5 пъти по-висока от плътността на тока измерена за мембранен електроден пакет с комерсиални електроди, която е 22-25 $mA.cm^{-2}$.
- ✓ Катализаторите Ni / Co / Mn, Co / Mn и Ni / Mn имат стабилни електрохимични характеристики при избраните експериментални условия.
- ✓ Най-високата скорост на двете частични електродни реакции е записана за CoMn: 160 $mA.cm^{-2}$ при катоден потенциал от -0,7 V и 58 $mA.cm^{-2}$, при аноден потенциал съответно 1,8 V. Тези стойности са по-високи от получените по-рано данни за каталитична активност на монометален Co, диспергиран върху същия носител. Тъй като кобалтът е добре известен със своята активност към OER, но не промотира HER, демонстрираната бифункционална активност на CoMn очевидно се дължи на наличието на Mn и интератомни взаимодействия между двата метала.

Благодарности: Национална Научна Програма „Нисковъглеродна енергия за транспорта и бита – ЕПЛЮС“, Договор Д01-2014/28.11.2018
Национална Научна Инфраструктура за производство и изследване на нови материали ИНФРАМАТ, Договор Д01-155/28.08.2018

ЕДИНАДЕСЕТА НАУЧНА СЕСИЯ
“МЛАДИТЕ УЧЕНИ В СВЕТА НА ПОЛИМЕРИТЕ” 10 СЕПТЕМВРИ 2020

Електроди за метал-хидрид (МХ) – въздух батерия, съдържащи тефлонизирани въглеродни материали

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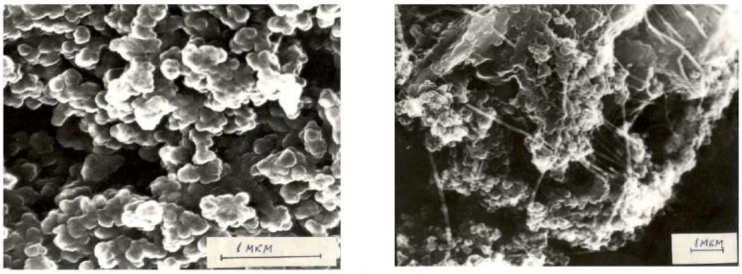
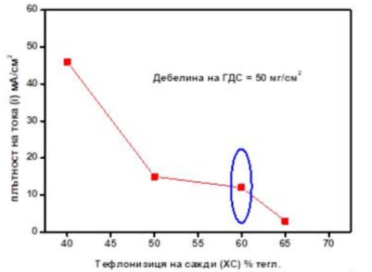
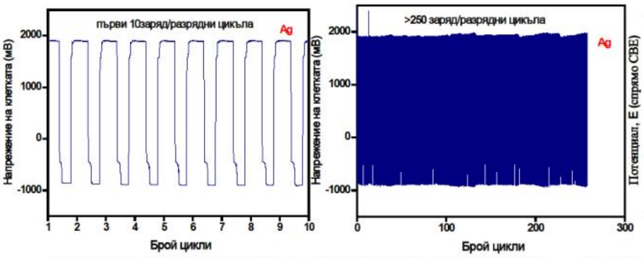
Акумулатор базиран на системите метал – въздух и/или метален хидрид-въздух е изключително перспективен, тъй като съчетава предимствата на никел-метал хидридните батерии от една стана и практически неограничения капацитет на кислородния електрод от друга. Преимуществата на една такава система са: висока плътност на енергията, висок капацитет, ниска цена и екологичност на изходните материали. През годините газодифузионният слой (ГДС) на електрода се приготвя от хидрофобен въглероден материал, модифициран с тефлон по създадена за целта технология, който осигурява механична стабилност на електрода. ГДС притежава висока пористост (около 0,9 cm^2/g), така че да осигури бърза дифузия и ефективно захранване с кислород. Поради високата си хидрофобност, той предотвратява изтичането на електролита през електрода. През 2016 година беше доразвита и усъвършенствана иновативна технология за тефлонизиране на въглеродни материали (сажди) с високо съдържание на тефлон, достигащо до 60 тегловни процента. Чрез така разработената технология се постигна и хомогенно разпределение на тефлона върху въгленовите частици.. Използването на тефлонизирани сажди е в основата на получаването на механически стабилни МХ и кислородни електроди. За направата на електродите бяха използвани хидрофобизирани сажди от тип Vulcan XC-72.



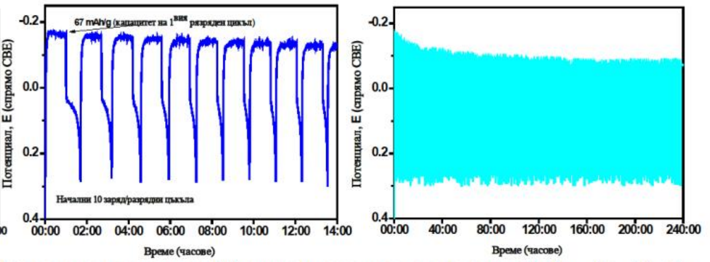
СЕМ микрофотография на изходен прах от VULCAN XC-72 (а) и (б) след тефлонизация



Зависимост на плътноста на тока от степентта на тефлонизация



Заряд/разрядна характеристика на ГДЕ с каталитичен слой от сребро



Заряд/разрядна характеристика на МХ електрод изготвен от сплав със състав $MmLa_{0.34}Ce_{0.66}Ni_{4.15}Fe_{0.85}$

Изводи

- **Максимални плътности на тока при кислородния електрод се получават при по-ниска степен на тефлонизация (около 40 тегл. %), достигащи над 40 мА/см^2.**
- **Продължителна работа в алкален разтвор изисква по-висока стабилност на кислородния електрод. За целта бяха изпозвани тефлонизирани 60 тегл. % сажди, при които токовите натоварвания достигат 10-15 мА/см^2, което е повече от достатъчно за поставените от нас цели за реализиране на демонстрационен прототип на батерия метал хидрид/въздух.**
- **Използването на тефлонизирани сажди е в основата на получаването на механично стабилни МХ и кислородни електроди, позволяващи постигането на над 200 заряд/разрядни цикъла.**

Благодарности

Работата се реализира с финансовата помощ на:
Националната научна програма "Нисковъглеродна енергия за транспорта и бита Е+ , финансирана от Министерство на образованието и науката Д01-214/29.11.2018
Център за Компетентност ХИТМОБИЛ Технологии и системи за генериране, съхранение и потребление на чиста енергия, проект № BG05M20P001-1.002-0014 се осъществява с финансовата подкрепа на ОП „Наука и образование за интелигентен растеж” 2014-2020, съфинансирана от ЕС чрез ЕФРР

Synthesis and characterization of N- and P- containing triethoxysilanes for modification of mesoporous particles

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INTRODUCTION

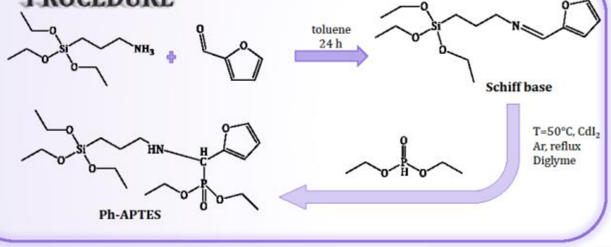
Silica materials are cheap, robust, and inert under most synthetic and catalytic conditions, but most importantly, the presence of silanol moieties on the surface allows for easy functionalization of the surface by condensation reactions or protonolysis. The incorporation of different functionalities on silica has been mostly designed through the post-modification of surfaces by tailored molecules containing a terminal trialkoxy- or trichlorosilane. Aminophosphonic acid derivatives with polar and conjugated groups can be attractive candidates for different industrial applications. The results presented in this poster concern studies focussed on the synthesis of N- and P- containing triethoxysilanes and their use for modification of mesoporous silicates.

SCHIFF BASES

METHODS

- A Schiff base was prepared from (3-aminopropyl) triethoxysilane (APTES) and furfural (Schiff base).
- An aminophosphonate derivative of APTES (Ph-APTES) was synthesized through addition of diethyl phosphite to the azomethine bond of the Schiff base using CdI_2 as catalyst
- The structures of the compounds were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

PROCEDURE

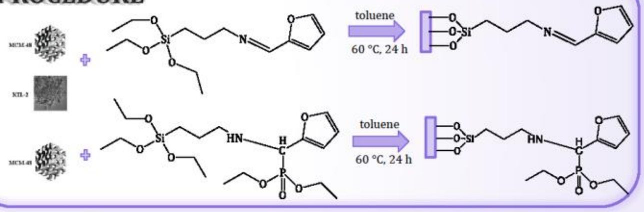


MESOPOROUS SILICATES

METHODS

- The mesoporous KIL-2 and MCM-48 materials were prepared by hydrothermal synthesis and characterized by XRD, TEM and nitrogen physisorption.
- Initial mesoporous silicas were modified with the Schiff base and Ph-APTES by post synthesis method.
- The modified mesoporous silicates were characterized by thermal analysis (TGA) and/or BET analysis in view of their application as sorbents for carbon dioxide.

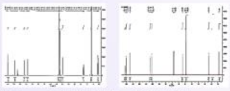
PROCEDURE



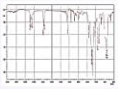
RESULTS

NMR-Result

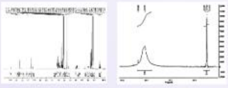
IR-Result



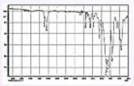
^{1}H and ^{13}C NMR of Schiff base



IR of Schiff base

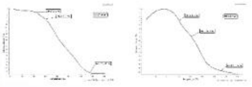


^{1}H and ^{31}P NMR of Ph-APTES

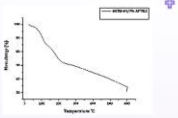


IR of Ph-APTES

TGA-Result



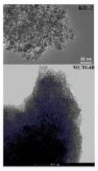
TGA curves of the modified silica KIL-2/A in air and argon



TGA curves of the modified silica MCM-48/Ph-APTES

RESULTS

TEM



N_2 physisorption data and CO_2 adsorption

Sample	S_{BET} m²/g	Pore volume cm³/g	Pore diameter nm	CO_2 adsorption mmol/g
KIL-2	545	1.48	14.5	1.2
KIL -2/A	485	1.20	14.0	1.8
MCM-48	980	0.80	2.5	1.5
MCM-48/A	880	0.66	2.3	5.8

The post-modification changed the characteristics of the silica materials

CONCLUSION

- Schiff base derived from APTES.
- The structure of Schiff base and Ph-APTES were proved by IR, ^{1}H and ^{31}P NMR spectral data.
- The mesoporous KIL-2 and MCM-48 materials were successfully prepared by hydrothermal synthesis.
- The modification of initial mesoporous silicas with Schiff base was performed by post synthesis method.
- The quantity of the incorporated organic modifier was about 40% determined by the TGA analysis.
- The modified mesoporous silicas show increased capacity for CO_2 adsorption depending on the peculiarity of the silica structure.

Acknowledgement

This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme E+: Low Carbon Energy for the Transport and Households, grant agreement D01-214/2018.

Постер 17

Thiol-ene coupling reaction achievement and monitoring by "*in situ*" UV-irradiation NMR spectroscopy

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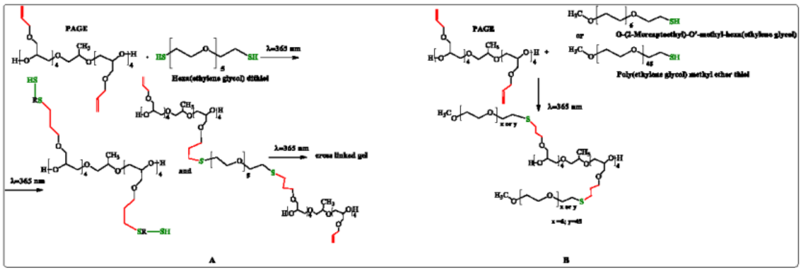
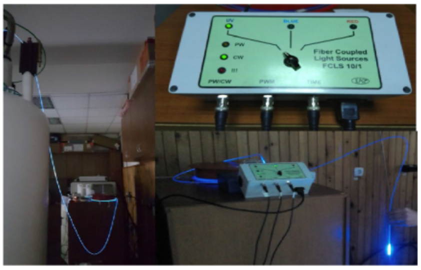
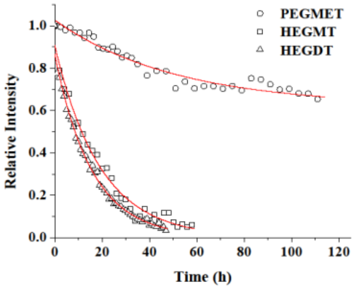
In this study, the possibilities of a new "*in situ*" LED UV illumination NMR spectroscopic technique for performing an initiator-free thiol–ene "click" coupling reaction of an allyl-functionalized poly(allyl glycidyl ether) (PAGE) prepolymer with a number of mono- and di-oligo polyethylene glycol (PEG) thiols is demonstrated. The state-of-the-art setup constructed with LEDs as UV light sources that illuminate through optical fibers directly into an NMR testing tube at a fixed wavelength of 365 nm. The selected experimental protocol uses a series of periods of irradiation and dark periods, thus providing opportunities to conduct an effective thiol–ene "click" reaction and simultaneously study the kinetics of the photochemical reaction with the exposure time, as well as macromolecular association directly in a solution applying the whole types of NMR methods: from conventional ^{1}H or ^{13}C NMR to diffusion NMR spectroscopy (DOSY). In addition, the molecular mass characteristics of the prepared copolymers were studied by gel-permeation chromatography (GPC).



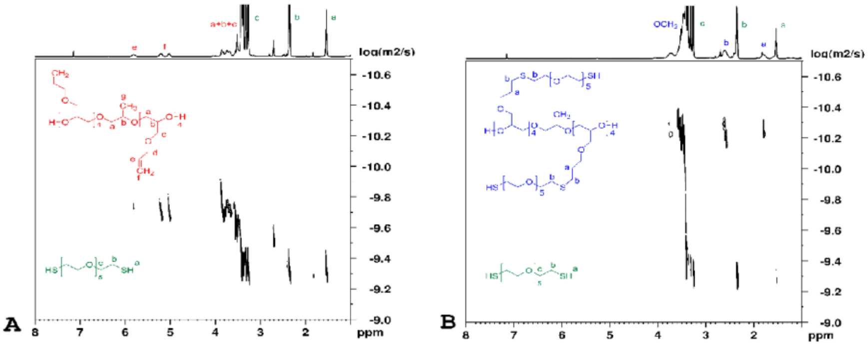
Synthesis of copolymers via thiol-ene "click" coupling reaction of PAGE and **A)** HEGDT ; **B)** HEGMT or PEGMET under "*in situ*" LED NMR irradiation at 365 nm without use of photoinitiator



LED control unit and optical fiber to the NMR tube used for "*in situ*" UV-irradiation NMR spectroscopy



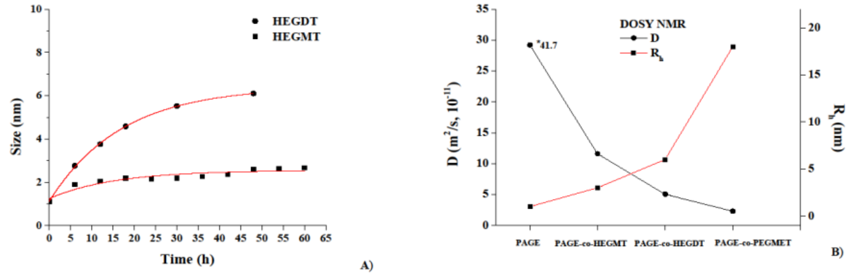
Consumption of C=C of PAGE in the course of LED UV-irradiation: **Δ)** HEGDT rate constant 1.8 x 10^{-5} s^{-1}; **☐)** HEGMT rate constant (1.1 x 10^{-5} s^{-1}, **O)** PEGMET rate constant 5.4 x 10^{-6} s^{-1}



^{1}H DOSY NMR spectra of **A)** PAGE and HEGDT reaction mixture before and **B)** after illumination at 365 nm for 48 h at room temperature, taken in C_6D_6 (600 MHz).

Sample	M_n^{GPC} [g.mol^{-1}]	Mw/Mn
PAGE	**1300**	**1.08**
HEGDT	-	-
HEGMT	**600**	**1.02**
PEGMET	**3600 (I)** **1600 (II)**	**1.04** **1.05**
PAGE-co-HEGDT	**5800**	**1.25**
PAGE-co-HEGMT	**3100**	**1.15**
PAGE-co-PEGMET	**9300 (I)** **4300 (II)**	**1.04** **1.06**

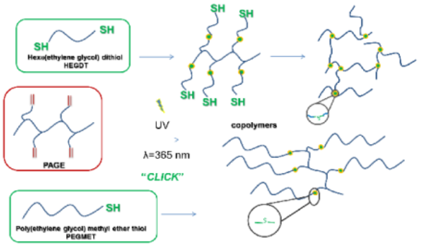
Characterization data of starting PAGE, HEMDT, HEGDT and PEGMET precursors and isolated copolymers



A) Change in hydrodynamic radius of PAGE-co-HEGDT and PAGE-co-HEGMT based species with the exposure time at RT. **B)** D and R_h values of PAGE prepolymer and PAGE-co-HEGDT, PAGE-co-HEGMT and PAGE-co-PEGMET based species after thiol-ene *"click"* coupling reaction, in C_6D_6 at RT.

*The value is taken at 40 °C.

Versatile UV-irradiated NMR spectroscopy for "*in situ*" study of coupling reaction of PAGE and few oligo-/PEG (di)thiols without any photoinitiator was successfully implemented. ^{1}H NMR spectra and GPC traces of resulting products after LEDs UV illumination support the expected turnaround of *"click"* reaction and formation of pegylated (co)polymers. The reaction efficiency depends on the type of thiol (mono or dithiol) at the selected PAGE molecular weight. Upon coupling with dithiol reagent, formation of a gel-fraction in a noticeable amount was observed, suggesting occurring of cross-linking reaction, which is subject of a further study. The observed differences in the reaction rates as well as in the size of species formed (the corresponding hydrodynamic radiuses R_h of aggregates) as a result of the coupling process of parent PAGE prepolymers and model PEG thiols were thoroughly examined and the reaction pathway proposed.



Acknowledgements: This work was financially supported by the Bulgarian National Science Fund (H 29/6) and by Ministry of Education and Science (INFRAMAT, D01-155).

Постер 18

Alternative approaches for determination of lignin molecular weight

Denitsa Nikolova[1,2], Albena Lederer[1]

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2. University Sofia, Faculty of Chemistry and Pharmacy

Introduction

- Part of lignocelluloses biomass;
- One of the most abundant biopolymers on Earth;
- Considered as a by-product of paper making industry;
- Major environmental pollutant;
- Its presents 300 billion tones and rising with almost 20 billion tones each year;

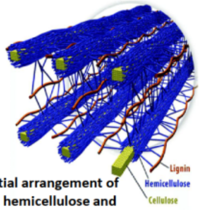
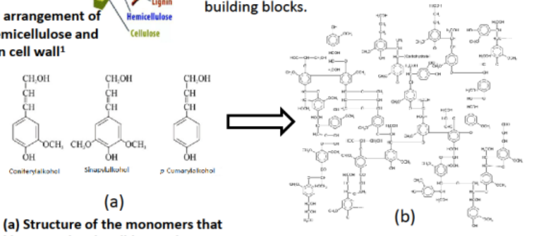


Fig.1. Spatial arrangement of cellulose, hemicellulose and lignin in cell wall[1]

- Renewable raw material;
- Presents between 27% and 37% of dry mass of vascular plants;
- Around 30% of the non-fossil organic carbon on Earth;
- Assumed as the largest natural source of aromatic building blocks.



(a)

(b)

Fig. 2. (a) Structure of the monomers that build lignin molecules; (b) Main lignin structure

- Different pulping procedure leads to differences in structure, respectively to differences in molar masses and physic-mechanical properties of obtained lignin;
- Acidic pulping- lignosulfonates; Alkalin pulping- kraft lignins and soda lignins, organosolv pulping, the Bergius-Reinau process, Steam explosion pulping, Separation by hydrolysis, etc.
- Made mainly from 3 monomers: Coniferyl alcohol, Sinapyl alcohol, p-Coumaryl alcohol;

The aims

The aim of this study was to develop a method for determination of lignin molecular weight, which have to be suitable for all kinds of lignin and at the same time affordable and easily accessible.

Difficulties in determination of lignin molecular weight

- Very hydrophobic;
- Not fully dissolved in organic solvents;
- No standards available;
- Fluorescence.

Determination molecular weights by size-exclusion chromatography (SEC)

Standard calibration

- Standards with exact molar mass;
- Made of the same substance or very similar;
- No available standards for lignin.

Multi angle light scattering (MALS)

- Measuring the scattered from the sample light;
- The radius of gyration;
- The refractive index increment dn/dc;
- Second virial coefficient A_2.

Determining the Refractive index increment- dn/dc

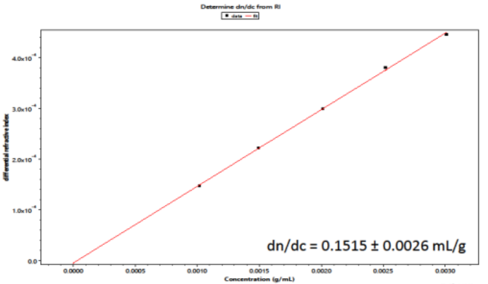


Fig. 3. Refractive index increment graph

The refractive index increment dn/dc is a constant value for the system sample-solvent. The solvent used for all experiments is dimethylacetamide (DMAc) with LiCl. The salt is added to the solvent to avoid interactions between the sample and the SEC column. The dn/dc value for the system lignin- DMAc with LiCl was found 0.155 ± 0.0026 mL/g. The fit of the line was R^2=0.9992.

Acknowledgement: *This work was kindly funded by Deutsche Bundesstiftung Umwelt*

1. A. Brandt, J. Gräsvik, J.P. Hallett, T. Welton, Deconstruction of lignocellulosic biomass with ionic liquids, Green Chem. 15 (2013) 550

SEC measurements

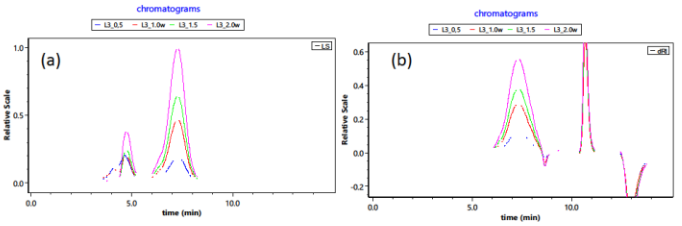
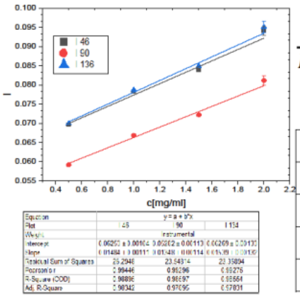


Fig. 4. Lignin chromatograms from (a) light scattering detector and from (b) refractive index detector

Calculating lignin molar mass



Equation	y = a + b*x		
Plot	I 45	I 90	I 134
Weight	Instrumental		
Intercept	0.06250 ± 0.00104	0.06202 ± 0.00113	0.06269 ± 0.00133
Slope	0.01484 ± 0.00111	0.01348 ± 0.00114	0.01539 ± 0.00132
Residual Sum of Squares	26.2948	23.54814	23.35894
Pearson's r	0.99446	0.99296	0.99275
R-Square (COD)	0.98896	0.98597	0.98554
Adj. R-Square	0.98342	0.97095	0.97831

Fig. 5. Plot intensity to concentration from 3 scattering angles

$$I \sim M_w . c . (\frac{dn}{dc})^2 + \mathrm{F}$$

$$\frac{I}{I-F} = \frac{M_{exp}}{M_{corr}} \Rightarrow M_{corr} = \frac{M_{exp} . (I-F)}{I}$$

Table 1. Experimental obtained molar masses

C[mg/mL]	M_{exp}[g/mol]
0.5	2.99 x 10^5
1	2.02 x 10^5
1.5	2.09 x 10^5
2	2.13 x 10^5

Table 2. Calculated molar masses

C[mg/mL]	M_{corr}[g/mol]
0.5	3.22 x 10^4
1	4.23 x 10^4
1.5	4.60 x 10^4
2	7.42 x 10^4

Figure 5 presents a plot of the measured intensity (I) against the concentrations (c) of used lignin solutions. It is known that the Intensity is proportional to the molecular weight (M_w), concentration and the square of refractive index increment (dn/dc). In the case of lignin, the intensity is also proportional of the fluorescence (F) (the intercept of the graph on Fig. 5). It is also known that the obtained intensity to the intensity minus fluorescence are threated as experimental obtained molar masses (M_{exp}) to the correction ones (M_{corr}). From this formula easily M_w can be calculated.

Fractionation of lignin sample

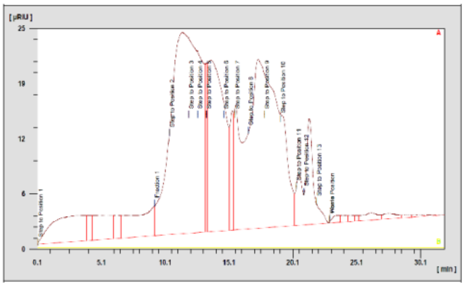


Fig. 6. Lignin fractionation chromatogram

To prove the results, obtained with correction formula, another method was supposed to be used. MALDI-TOF-MS was planed. For this purpose, first fractionation of lignin sample was proceed. 10 different fractions were collected. MALDI-TOF-MS measurements are still in progress.

SEC measurements of the fractions

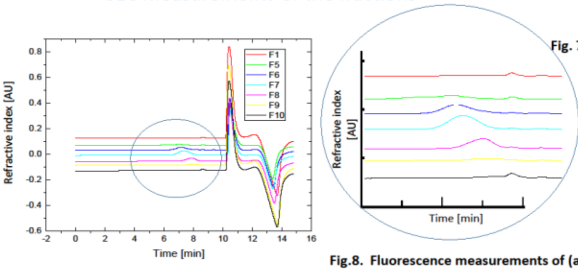


Fig. 7. SEC-chromatograms of the lignin fractions

Fluorescence measurements

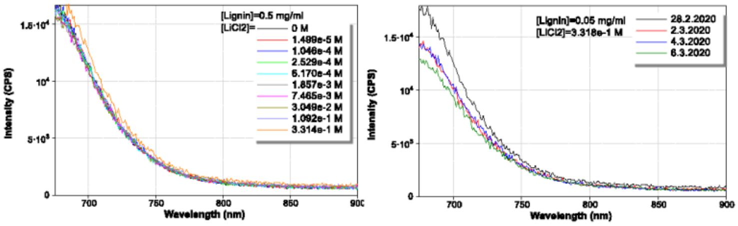


Fig.8. Fluorescence measurements of (a) lignin with different concentrations of LiCl and (b) lignin with LiCl after within one week at excitation wavelength 661 nm

Биоразградими криогелове получени чрез термично-индуцирано омрежване на 2-хидроксиетилцелулоза с лимонена киселина

<u>Надежда Бозова</u>, Петър Д. Петров

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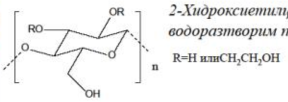
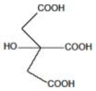
През последните десетилетия природните полимери намират все по-широко приложение за направата на различни изделия с приложение в медицината и фармацията поради своята достъпност, нетоксичност, биоразградимост и ниска цена. Производните на целулозата са водоразтворими полимери, често използвани за получаване на различни биоматериали, включително хидрогелове.

Целта на това проучване е да се разработи метод за омрежване на криоструктурирана 2-хидроксиетилцелулоза в отсъствие на опасни за здравето реагенти.

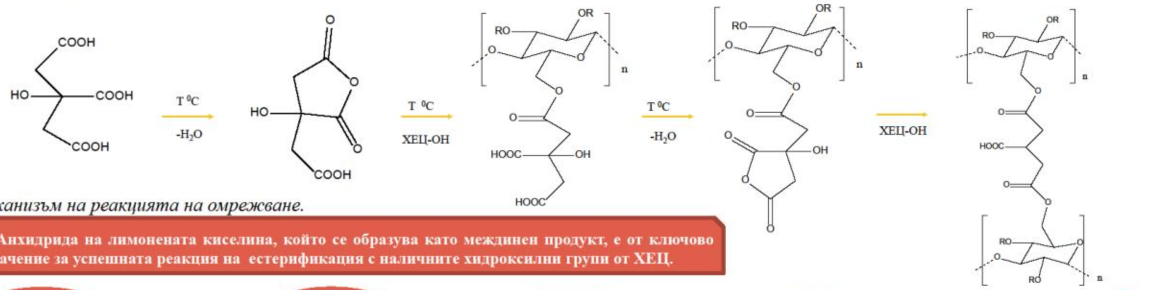
Реагенти:



2-Хидроксиетилцелулоза /ХЕЦ-ОН/ - водоразтворим полимер от природен произход.



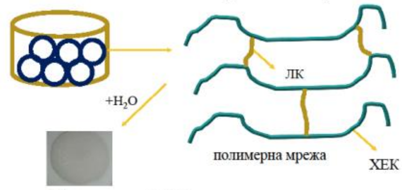
Лимонена киселина /ЛК/ - слаба органична киселина, съдържа се в цитросовите плодове. Участва в метаболизма на почти всички живи същества .



Фиг.1 *Механизъм на реакцията на омрежване.*

Анхидрида на лимонената киселина, който се образува като междинен продукт, е от ключово значение за успешната реакция на естерификация с наличните хидроксилни групи от ХЕЦ.

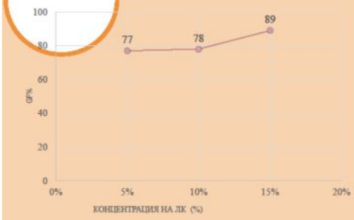
Фиг. 2 *Схематично представяне на процеса на получаване на криогел.*



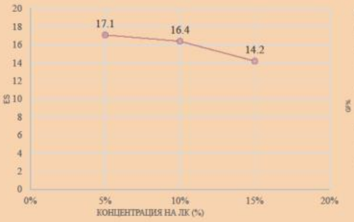
Фиг. 3. *Криогел от ХЕЦ омрежена с лимонена киселина*

За получаване на криогеловете е използван 2 wt % воден разтвор на 2-хидроксиетилцелулоза и три различни концентрации на лимонената киселина /5%, 10%, и 15%, спрямо ХЕЦ/

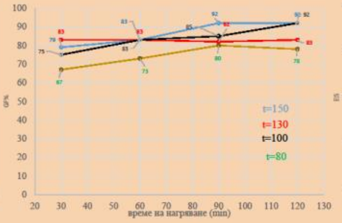
Резултати:



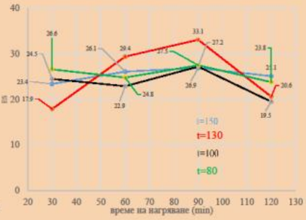
Фиг. 4. Зависимост на добива на гел фракция (GF) от концентрацията на лимонената киселина. Реакцията е проведена при нагряване за 10 мин. при температура 180^0C.



Фиг. 5. Зависимост на степента на набъбване (ES) от концентрацията на лимонената киселина. Реакцията е проведена при нагряване за 10 мин. при температура 180^0C

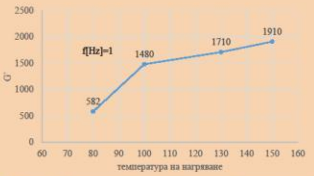


Фиг. 6. Зависимост на GF от времето на нагряване и от температурата на нагряване.



Фиг. 7. Зависимост на ES от времето на нагряване и от температурата на нагряване.

Фиг. 8. Зависимост на модула на еластичност (G`) от концентрацията на лимонената киселина. T = 180^0C.



Фиг. 9. Зависимост на модула на еластичност от температурата на нагряване. 15 % ЛК.

При по-висока концентрация на ЛК реакцията на омрежване протича с по-висока ефективност, в резултат на което са получени криогелове с по-високи GF и G`. Температурата и времето на нагряване са другите два параметъра, които влияят върху омрежването и съответно върху свойствата на криогеловете.

Фиг. 10. Лиофилизиран ХЕЦ-ОН

1. Нагряване при 70^0C
2. $+H_2O$

Фиг. 11. ХЕЦ-ОН във вода /начало/

След 1 ден

Фиг. 12. Разтвор на ХЕЦ във вода

Чрез контролен експеримент е доказано, че в отсъствие на ЛК не протича омрежване на ХЕЦ-ОН при дадените реакционни условия.

Изводи: Успешно е омрежена криоструктурирана хидроксиетилцелулоза с помощта на лимонена киселина в твърда фаза, след лиофилизация на воден разтвор. Реакцията на омрежване протича с висока ефективност при температура над 70 ^0C в рамките на 30 мин. Получените ХЕЦ криогелове са еластични материали със супер-макропореста структура.

Постер 20

ЕДИНАДЕСЕТА НАУЧНА СЕСИЯ
"МЛАДИТЕ УЧЕНИ В СВЕТА НА ПОЛИМЕРИТЕ" 10 СЕПТЕМВРИ 2020

Hydrogen economy based on advanced materials for hydrogen storage, battery and fuel cell application

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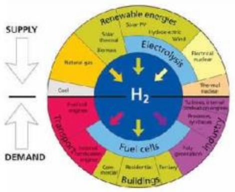
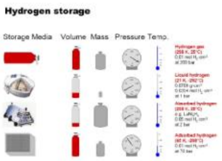
Hydrogen is frequently regarded as one of the best ways to store energy produced by renewable power sources which have an intermittent character. The rising capacity of localised and dispersed renewable energy sources (RES), exceeding the gigawatt range, require a proportional storage system to be set up. At normal conditions, hydrogen, on a volume basis, is practically comparable to other fuel carriers such as gasoline and natural gas. Furthermore, in order to achieve a sustainable hydrogen economy and completely replace fossil fuels significant technical challenges have to be addressed and overcome in different areas: production and generation, storage and conversion to electrical energy and heat.

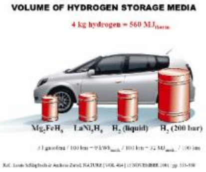
This presentation gives an overview on how hydrogen may be produced and stored, having in mind its environmental protection added value, in comparison to other techniques.

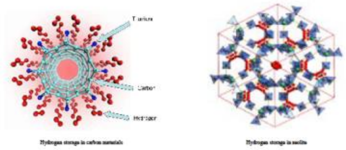
Current methods for energy storage include: compressed gas, cryogenic liquid, solid metal hydrides, high porosity nanostructure zeolite, and others but the different technologies are suited for different applications. Metal hydrides (MH)s, for instance, have advantages in terms of the requirements of operating temperature, pressure and energy in comparison to other storage materials. They are heavy but weight is not a big issue for stationary and niche applications, including emergency energy supply and black start.



https://www.hornerautomation.eu/horner-ocs-application-in-the-production-of-hydrogen/



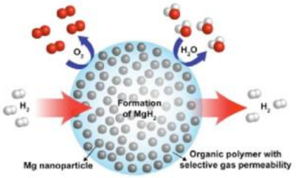




Hydrogen storage in carbon materials

Hydrogen storage in zeolite

Tomáš Brestovič, Natália Jasminská, Marián Lázár, Ľubica Bednárová, and Romana Dobáková, "The possibilities of obtaining hydrogen from renewable energy sources and its subsequent storage," *International Research Journal of Advanced Engineering and Science*, Volume 2, Issue 4, pp. 6-11, 2017



In 2011, scientists at the Lawrence Berkley National Laboratory developed a composite material based on magnesium nanoparticles embedded in a flexible organic polymer matrix. The material is capable of selectively absorbing hydrogen gas, storing it safely at such high densities as magnesium hydride, and releasing it rapidly when required. Photocatalytic production of hydrogen from water and storage of hydrogen using innovative nanomaterials may become the basis of a feasible distribution infrastructure, efficiently allowing vehicles and local combined heat and power (CHP) systems to run on solar energy, stored as clean and efficient hydrogen fuel. Moreover, polymer electrolyte membrane (PEM) electrolysis provides a sustainable solution for the production of hydrogen, and is excellently suited to couple with RES energy sources such as wind and solar.

A good example is the work and investment done by the Hanwha Energy Business Group which has recently built the first power station in the world for hydrogen fuel cells which generates electricity using excessive amounts of hydrogen byproduct and thus, achieving the aim of a sustainable "circular economy".

A hydrogen economy based on different innovative technologies and techniques for production and storage of hydrogen, using novel polymer containing materials, is a cornerstone for the future energy efficiency targets of the EU and the pursuit for energy independence. This work is part of research conducted in the frame of the projects E+ (Low Carbon Energy for the Transport and Households) and Centre of Competence HITMOBIL (Technologies and Systems for Generation, Storage and Consumption of Clean Energy).

Hanwha Energy - Power Plants with fuel cell - Hydrogen fuel in circular economy

Nel Hydrogen Electrolyser, a division of Nel ASA (Nel, OSE:NEL), has received a purchase order for a 2 megawatt (MW) containerized Proton PEM® electrolyzer, as part of a 30 MW framework agreement with Hydrospider AG, an affiliated company of H2 Energy. The electrolyzer will be used to produce green hydrogen for heavy-duty hydrogen trucks from Hyundai Motor Company, which will begin operation in Switzerland during late 2019. The framework agreement represents the first phase of 60 – 80 MW needed to supply hydrogen for the total expected 1,000 trucks and other applications.

Acknowledgements

This work was supported by the Bulgarian Ministry of Education and Science under the National Research Program E+: Low Carbon Energy for the Transport and Households, grant agreement D01-214/2018;

Center of competence HITMOBIL - Technologies and Systems for Generation, Storage and Consumption of Clean Energy", No BG05M20P001-1.002-0014

Rapid and initiator-free conjugation of oligonucleotides via UV light-induced thiol-ene click reaction

P. Denkova, K. Kostova, E. Dimitrov, N. Toncheva-Moncheva, P. Bakardzhiev, S. Rangelov

Химикотехнологичен и металургичен университет - София

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BULGARIAN ACADEMY OF SCIENCES

Abstract: Spherical nucleic acids (SNAs) are nanostructures, composed of highly oriented and densely grafted oligonucleotides on the surface of a nanoparticle which can be inorganic, hollow or organic. The dense three-dimensional arrangement of the oligonucleotides imparts unique advantages over traditional nucleic acid delivery methods, including cellular uptake with no need of transfection agents, resistance to nuclease degradation and ability to overcome different biological barriers. SNAs with hollow architectures are one of the new forms of SNAs. These particles consist of liposomal cores composed of phospholipids, the surface of which is functionalized with DNA strands, modified with a hydrophobic residue, which intercalates into the phospholipid bilayer. In this study we develop a novel synthetic route for preparation of a conjugate to be intercalated in the phospholipid bilayer. The conjugate consists of a lipid-mimetic anchor to which an oligonucleotide strand is attached. The conjugation is performed by an initiator-free, UV light-induced thiol-ene click reaction in mild conditions not harmful for the nucleic acid.

Key words: Nucleic acid-polymer conjugates, Thiol-ene "*click*" reactions, spherical nucleic acids, cell internalization, UV-irradiation, Poly(allyl glycidyl ether)

Strategy benefits for oligonucleotide based conjugate preparation using a new UV set up:

- ✓ One simple reaction step.
- ✓ Mild reaction conditions.
- ✓ Initiator-free system.
- ✓ Use of environmentally friendly solvents.
- ✓ Use of LEDs as UV light sources emitting at fixed 365 nm wavelength which is appropriate for various polymeric and biological materials as well as functional oligonucleotides.
- ✓ Rapid and highly ffective thiol-ene "click" reaction directly in solution:
- ✓ Quantitative yields, regioselectivity.

Synthesis:

UV set up

Figure 1. The UV set up emitting at 365 nm fixed wavelength, with six LED-diodes (4 W maximum capacity).

Table 1. Characterization data of the oligonucleotide used (Biomers).

Code	Oligonucleotides composition* Sequence (5′→3′)	Mw (g.mol^{-1})	Ext. Coeff.
ThiolC6-oligo	Thiol-C_6-(spacer 18)$_1$ ta ata cga ctc act ata gg	6670	230600

C6 = $(CH_2)_6$ groups, spacer18 denotes a phosphodiester followed by 6 ethylene glycol units in the DNA backbone

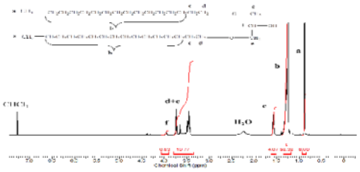
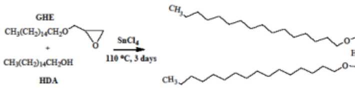


Figure 2. ^{1}H-NMR spectrum of DHP (Mn=540 g.mol^{-1}) in $CDCl_3$

Synthesis of DHP (Mn=540 g.mol^{-1})

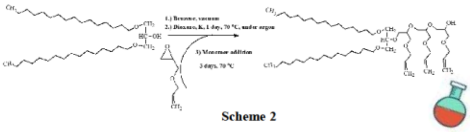
(DHP – dihexadecyl-propan-2-ol) was obtained from glycidylhexadecyl ether (GHE, Mn=298,5 gr.mol^{-1}), 1-Hexadecanol (HDA, Mn=242,44 g.mol^{-1}) and $SnCl_4$(260.52 g.mol^{-1}) (Scheme 1).



Scheme 1

Synthesis of DHP-co-PAGE$_3$ macroagent (Mn=882 g.mol^{-1})

DHP-co-PAGE$_3$ was obtained by anionic polymerization of AGE (allyl glycidyl ether) monomer. The number (n=3) of allyl polyglycidyl ether) (PAGE) functional units was calculated from HNMR spectrum.



Scheme 2

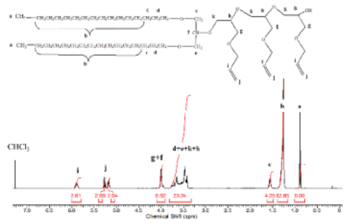
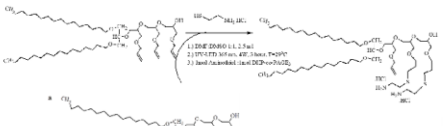


Figure 3. ^{1}H-NMR spectrum of DHP-co-PAGE$_3$ macroagent (Mn=882 g.mol^{-1}) in $CDCl_3$.

Reference synthesis 1:

1) Synthesis of DHP-co-PAGE$_3$–co-2-Aminoethanethiol hydrochloride (AT) (Scheme 3)



Scheme 3

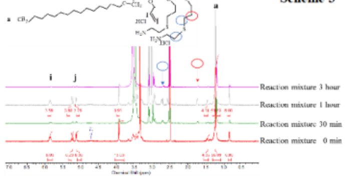
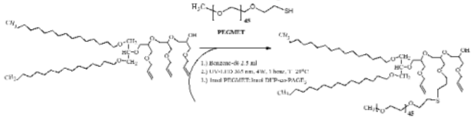


Figure 4. HNMR spectra ofDHP-co-PAGE$_3$ and AT, before (0 min) and after (30 min, 1 hour and 3 hours illumination at 365 nm, 4W, taken in DMSO-d6 (600MHz).

Reference synthesis 2:

2) Synthesis of DHP-co-PAGE$_3$–co-PEGMET(Scheme 4)



Scheme 4

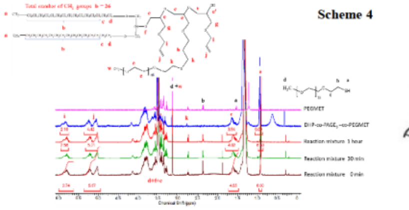
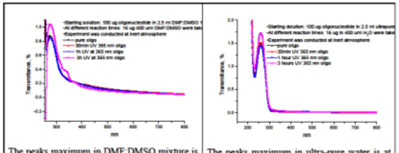


Figure 5. HNMR spectra ofDHP-co-PAGE$_3$ and PEGMET reaction mixture, at 0 min, 30 min, 1 hour illumination at 365 nm 4W and after purification of DHP-co-PAGE$_3$ –co-PEGMET product obtained for 1 hour, taken in DMSO-d6 (600MHz).

Reference experiment 3:

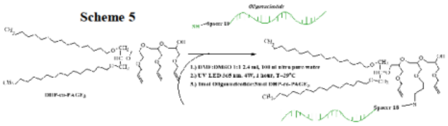
3) Pure Oligonucleotides UV illumination at 365 nm, 4W (100% capacity of the UV lamp) for different reaction times



The peaks maximum in DMF:DMSO mixture is at 275 nm.	The peaks maximum in ultra-pure water is at 260 nm.

The oligonucleotide is stable until 1 hour UV illumination at 365 nm 4W, inert atmosphere.

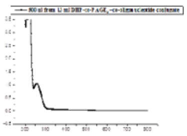
4: Synthesis of DHP-co-PAGE$_3$–co-oligonucleotide conjugate (Scheme 5), Yeld$_{theor}$=552.14 μgr, Yeld=330.03 μgr



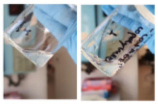
Scheme 5

DHP-co-PAGE$_3$-co-oligonucleotide after dialysis in 13ml ultrapure water
A_{260}=1.0598

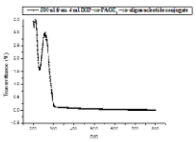
Concentration = 30.63 μgr/ml



DHP-co-PAGE$_3$-co-oligonucleotide after dialysis in 750 ul and 4 ml ultrapure water
A_{260}=2.8979



Concentration = 83.75 μgr/ml



Gel-electrophoresis (Figure 6):

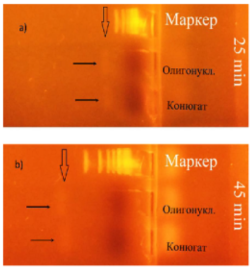


Figure 6. Agarose gel retardation analysis of functionalized oligonucleotides andDHP-co-PAGE$_3$-co-oligonucleotide conjugate. (a) Duration of the experiment 25 min., (b) Duration of the experiment 45 min. The arrows indicate appearance of bands associated with formation of a second fraction of particles which are retained at the starting line.

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ПРЕБИОТИЧНО ОБРАЗУВАНЕ НА ХИПОКСАНТИН ОТ ФОРМАМИД

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ВЪВЕДЕНИЕ

Пребиотичните реакции, основаващи се на химията на формамида, са насочени към разбирането как от по-прости съединения може да се стигне до информационно-съхраняващи полимери – ДНК и РНК. Въпросът как нуклеобазите са се образували от малки пребиотични молекули в извънземна среда предизвика голям интерес.

Нуклеобазата хипоксантин е включена в нуклеозида инозин, който се намира в тРНК и е от съществено значение за правилното превеждане на генетичния код. В експерименталната работа на Lagoja и Herdewijn[1], е показано, че хипоксантин може да се образува от карбамид, мравчена киселина и глицинамид.

Цел на представеното теоретично изследване е намиране на реакционния път, по който се получава хипоксантин от карбамид в кондензирана среда, която играе роля на катализатор и установяване на механизмите, по които се извършват реакциите.

МЕТОДИ

За моделиране на механизма на реакциите и оптимизация на геометриите на реагентите, продуктите и преходните състояния са проведени *ab initio* SCS-MP2/cc-pVDZ квантово-химични изчисления. Всички изчисления са извършени с използване на програмата GAMESS.

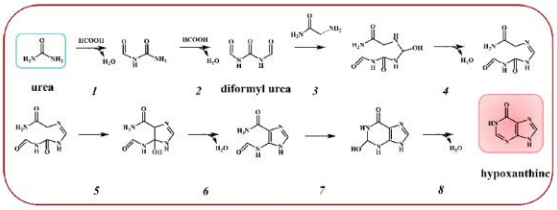
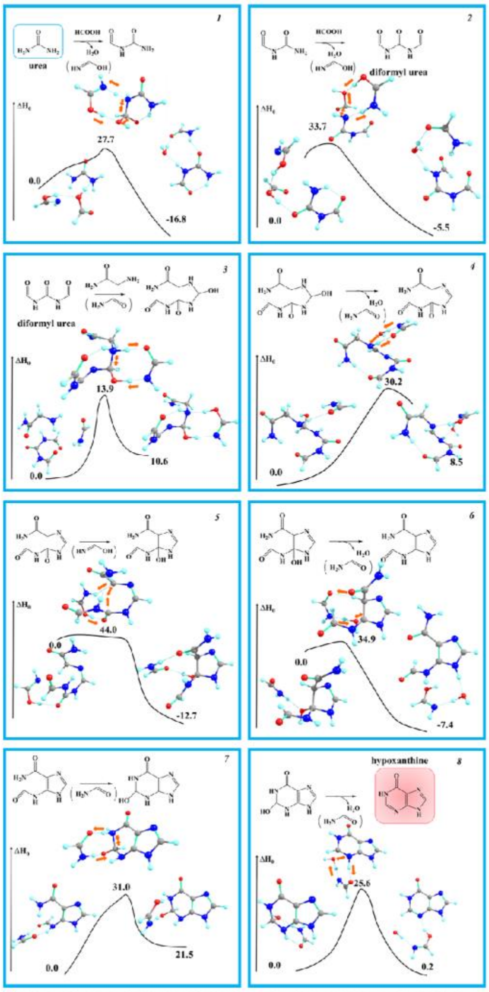
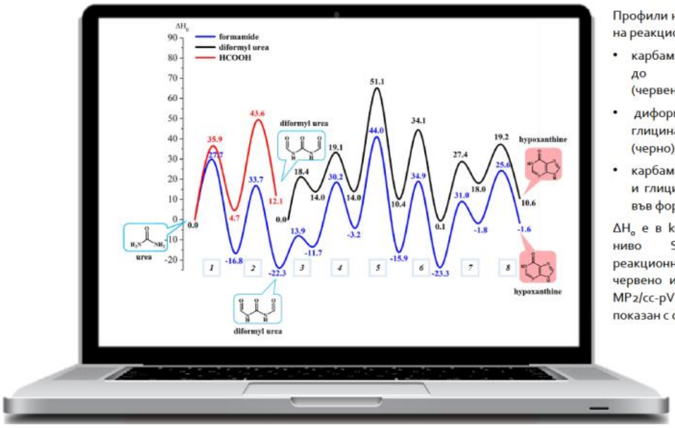


Схема на реакционен път от карбамид и глицинамид до хипоксантин. За всека реакция реагентът е изобразен над стрелката.

РЕЗУЛТАТИ



Оптимизирани структури на реагенти и продукти и енергетичен профил на реакционния път на образуване на хипоксантин от карбамид (стъпки 1-8). ΔH_0 (Et + ZPVE) е в kcal mol⁻¹, изчислени на теоретично ниво SMD/MP2/cc-pVDZ .



Профили на потенциална енергия на реакционен път от:

- карбамид и мравчена киселина до диформилкарбамид (червено);
- диформилкарбамид и глицинамид до хипоксантин (черно);
- карбамид, мравчена киселина и глицинамид до хипоксантин във формамид (синьо).

ΔH_0 е в kcal mol⁻¹, изчислена на ниво SCS-MP2/cc-pVDZ за реакционните пътища, показани в червено и черно, и с SMD/SCS-MP2/cc-pVDZ за реакционният път показан с синьо.

ИЗВОДИ

За първи път е предложен реакционен път за образуване на хипоксантин от карбамид, мравчена киселина и глицинамид в среда от формамид и по логичен начин може да се стигне до нуклеобазата хипоксантин, която играе важна роля за получаване на информационните полимери ДНК и РНК.

БЛАГОДАРНОСТИ

Тази работа е подкрепена от МОН чрез Национална Програма „Млади учени и постдокторанти", одобрена от DCM # 577 /17.08.2018.

Пресмятанията са извършени с помощта на изчислителен комплекс АВИТОХОЛ, Център за иновативни пресмятания и обработка на данни – БАН.

ЛИТЕРАТУРА

[1] I. M. Lagoja, P. Herdewijn, Chem. Biodiversity, 2004, 1, 106-111

Thermoresponsive properties and levofloxacin loading capacity of star shaped poly(N-isopropylacrylamides)

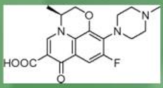
__Silvia Bozhilova__, Sijka Ivanova, Darinka Christova
Institute of Polymers – Bulgarian Academy of Sciences

BACKGROUND

Poly(N-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer, that exhibit a drastic and discontinuous change of physical properties with changing the temperature in aqueous solution. At about 32 °C PNIPAM macromolecules undergo coil-to-globule phase transition and separate from water molecules. The transition temperature is called cloud point (T_{cp}) and is concentration-dependent, PNIPAM undergo a phase transition near to physiological human body temperature witch makes it suitable for biomedical applications such as drug delivery.

Levofloxacin is a synthetic fluorinated quinolone derivative, well soluble in aqueous media. Levofloxacin is an antibiotic active against most of the aerobic Gram-positive and Gram-negative organisms and demonstrates moderate activity against anaerobes. Like most antibiotics, there is no selective targeting of Levofloxacin towards pathological site which could restrict its antibacterial efficacy. This challenge could be overcame by loading of the drug molecule in suitable polymeric carrier.

Chemical structure of Levofloxacin



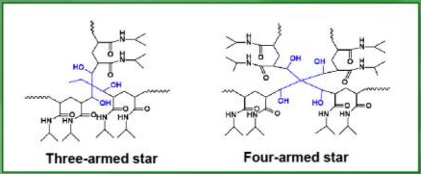
The aim of this study is to explore temperature-responsive properties in aqueous solution of star-shaped PNIPAMs and to examine their loading capacity towards the antibiotic Levofloxacin

RESULTS

Star-shaped PNIPAM polymers were synthesized by redox polymerization of N-isopropylacrylamide (NIPAM) using cerium ammonium nitrate (CAN) as an initiator and different hydroxyl-precursors: 1,1,1-tris(hydroxymethyl)-propane (THMP) as the initiating center for the three-armed star polymer and pentaerythritol (PER) for the four-armed star polymer. The polymerization was carried out under a nitrogen atmosphere at mild reaction conditions - aqueous medium at 35 °C. Copolymer composition and structure were studied by Proton Nuclear Magnetic Resonance (^{1}H NMR) and Furrier Transformed Infrared (FTIR) spectroscopy. Thermoresponsive properties were evaluated in dilute aqueous solutions by UV-VIS transmittance measurements at increasing temperature

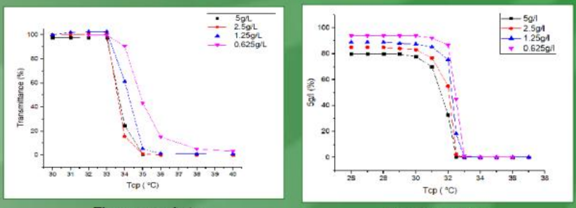
The loading of Levofloxacin was performed at temperature 25°C on a magnetic stirrer for 3 hours. The loading capacity and entrapment efficiency (EE) were determined using indirect UV-VIS analisys. The encapsulation efficiency (EE%) is defined by the concentration of the incorporated drug detected in the formulation over the initial concentration used to make the formulation. Loading capacity (LC%) can be calculated by the amount of total entrapped drug divided by the total nanoparticle weight.

Molecular structures of the obtained star-shaped PNIPAMs



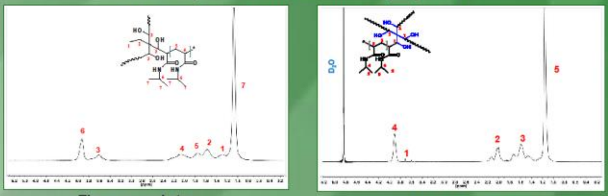
Three-armed star Four-armed star

Clouding curves registered at 500 nm used to determine T_{cp}



Three-armed star Four-armed star

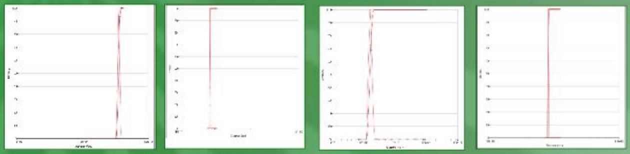
^{1}H NMR spectra of the obtained copolymers



Three–armed star Four–armed star

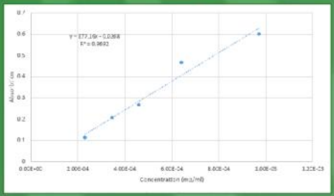
DLS analysis

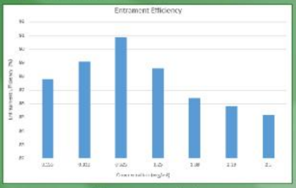
Polymer	T(°C)	Eff. Diam. (nm)	Dispersity
Three-armed star	27	76.22	0.297
	39	347.29	0.047
Three-armed star/Levo	25	35.33	0.492
	39	190.32	0.093
Four-armed star	25	53.17	0.200
	39	161.55	0.011
Four-armed star/Levo	25	40.07	0.272
	39	161.46	0.003



Three-armed star Three-armed star/Levo Four-armed star Four-armed star/Levo

Levofloxacin loading to PNIPAM

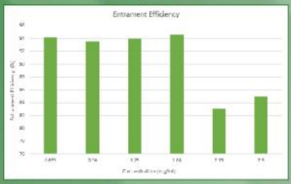




Three–armed star

Levofloxacin calibration curve and equation

$$\mathrm{EE}(\%) = \frac{\text{total drug} - \text{free drug}}{\text{total drug}} \times 100$$



Four-armed star

CONCLUSIONS

The obtained star-shaped PNIPAM polymers show a phase separation behaviour similar to the linear PNIPAM. Because of their specific three-dimensional architecture and their unique properties in aqueous solution, obtained copolymers have potential in biomedical field as drug delivery carriers. The obtained results for drug loading efficiency show a high sorption capacity of star-shaped PNIPAM polymers toward Levofloxacin.

ACKNOWLEDGMENTS

S. Bozhilova acknowledges Bulgarian Ministry of Education and Science for support under the National Research Programme "Young scientists and postdoctoral students" approved by DCM # 577 / 17.08.2018.

Изследване потенциала на различни PEO-PCL мицелни системи за разтваряне на хидрофобни биологично активни вещества

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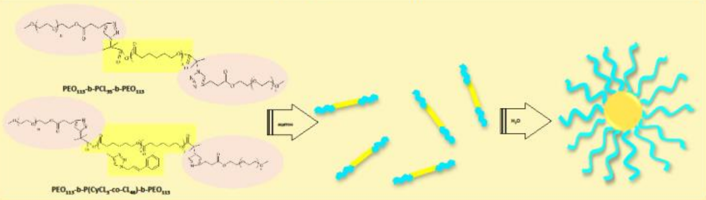
Увод

Наномедицината е раздел от науката медицина, който дава нови възможности при формулирането и доставянето на лекарствени вещества. Тя прави постижими промени във факмакокинетиката, които позволяват лесно преминаване през биологичните бариери, подобрен терапевтичен ефект и селективно доставяне на биологично активните вещества (БАВ).

Целта на това проучване е да се сравни потенциала на две мицелни системи, получени от съполимери на поли(етиленов оксид) (PEO) и поли(ε-капролактон) (PCL), като носители на хидрофобни БАВ. Съполимерите се различават по това, че при единия от тях хидрофобния PCL блок е модифициран и съдържа висящи цинамилни групи.

Самоасоцииране на амфифилни триблокови съполимери



Фиг. 1: Получаване на мицелен разтвор от двата изследвани съполимера

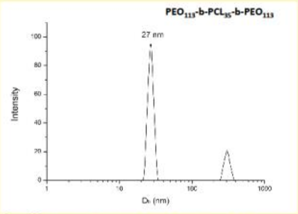
Таблица 1. Молекулно-масови характеристики на триблоковите съполимери.

Съполимер (код)	$M_n^{1H\text{-}NMR}$ (g mol^{-1})	M_n^{GPC} (g.mol^{-1})	M_w/M_n	MF[1] (%)
PEO_{113}-b-P($CyCL_3$-co-CL_{46})-b-PEO_{113} (GEGR)	15700	8800	1.13	6
PEO_{113}-b-PCL_{35}-b-PEO_{113} (MAGA)	14400	9400	1.08	0

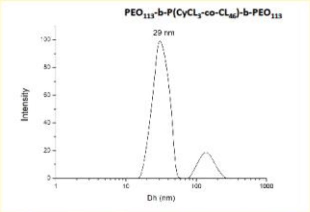
[1]MF - Молна фракция на α-цинамил-ε-капролактон

Приготвени бяха мицелни разтвори с концентрация 2,5 g/L чрез метода изпаряване на разтворителя

Охарактеризиране и натоварване с БАВ



Фиг. 2: Разпределение по размер на полимерните мицели, получени от **PEO_{113}-b-PCL_{35}-b-PEO_{113}**



Фиг. 3: Разпределение по размер на полимерните мицели, получени от **PEO_{113}-b-P($CyCL_3$-co-CL_{46})-b-PEO_{113}**

Таблица 2. Физико-химични характеристики на полимерните мицели получени от амфифилни триблокови съполимери.

Съполимер	Хидродинамичен диаметър (nm)	ζ – потенциал (mV)
PEO_{113}-b-PCL_{35}-b-PEO_{113}	27	- 6,7
PEO_{113}-b-P($CyCL_3$-co-CL_{46})-b-PEO_{113}	29	- 1,3

Чрез динамично разсейване на светлината (DLS) бе определено, че двата съполимера формират близки по размер мицели

При еднакви експериментални условия мицелите бяха натоварени с активното вещество при масови съотношения носител/БАВ 5:1, 10:1, 15:1 и 20:1 .

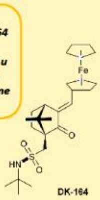
фазово разделяне при съотношение 10:1

разтворът при съотношение 20:1 все още е колоидно стабилен

Фиг. 4: Дигитални снимки на натоварени с активно вещество мицелни системи, заснети по различно време след натоварването.

Фиг. 5: Дигитални снимки на стабилните във времето системи.

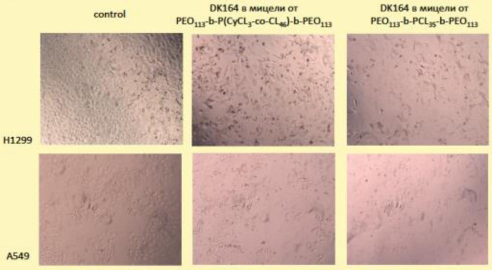
Мицелите натоварени с DK164 при масово съотношение 15:1 и 20:1 са колоидно стабилни в рамките на 20 h.



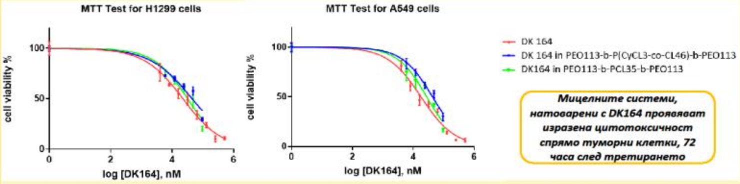
DK-164

Фиг. 6: Структурна формула на използваното активно вещество.

Цитотоксичност



Фиг. 7: Микроскопски наблюдения на клетки третирани с 128 μM DK164, натоварен в полимерните системи, за 72 ч.



Мицелните системи, натоварени с DK164 проявяват изразена цитотоксичност спрямо туморни клетки, 72 часа след третирането

Фиг. 8: Резултати от МТТ анализ за цитотоксичното действие на чист и натоварен в мицели DK164 (съотношение 20:1). H1299 и A549 клетки са третирани за 72ч.

Заключение

Биологично активното вещество DK-164 успешно е солюбилизирано в наноразмерни мицелни носители, получени чрез самоасоцииране на амфифилни PEO_{113}-b-PCL_{35}-b-PEO_{113} и PEO_{113}-b-P($CyCL_3$-*co*-CL_{46})-b-PEO_{113} блокови съполимери. Разтворите на натоварените мицели и от двата полимера са колоидно стабилни при концентрация на полимера 2,5 g/L и масово съотношение съполимер/БАВ 15:1 и 20:1. Първоначалните резултати показват, че модифицирания полимер няма видимо по-добър потенциал за солюбилизиране на DK-164.

NOVEL PHOTOACTIVE POLYMER COATINGS: PROPERTIES AND ANTIBACTERIAL ACTIVITY

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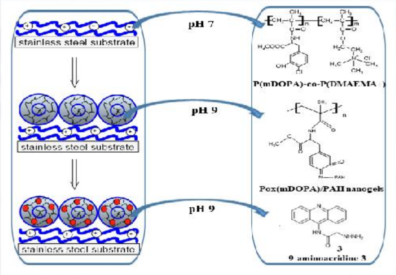
INTRODUCTION

The surfaces that release antibacterial compounds are effective, although ultimately they can be exhausted. Moreover, the used antibacterial agents present a potential problem due to the possibility of occurring bacterial resistance, which is a result from the continuous release of active compounds into the environment for a long period of time. Other type of surfaces is those that kills bacteria in contact and does not continuously release biocides. Such surfaces contain copper or silver ions, but currently they still have not found real application in the clinical practice. One novel and innovative alternative represents surfaces that catalytically produce bactericides using externally applied chemical, electrical or optical energy. To this group belong light-activated antimicrobial coatings. At the present exactly those coatings attract considerable research interest, due to the possibility of continuous disinfection of the surface, overcoming the disadvantages of the other coatings. This process is a result of irradiation of certain compounds with visible light (so called photosensitizers) that lead to the production of cytotoxic components such as singlet oxygen and free radicals as a result of the occurring photodynamic processes. These highly reactive species are responsible for the destruction of the attacked cells.

RESULTS AND DICUSSION

Formation of photoactive polymer coatings on stainless steel (SS)

The formation of photoactive polymer coating on SS was based on "all-in-one" approach, thus reducing the need of multilayer depositions which can affect the processing rate and to reduce the production costs (Scheme 1).



Scheme 1. Schematic representation of the preparation of photoactivate polymer coatings: first layer - P(mDOPA)-co-P(DMAEMA+) copolymer; second layer: P(mDOPA)-co-P(DMAEMA+)/Pox(mDOPA)/PAH; third layer: P(mDOPA)-co-P(DMAEMA+)/Pox(mDOPA)/PAH/9-aminoacridine 3.

Quartz Crystal Microbalance coupled with Dissipation (QCM-D)

The deposition of all layers and formation of photoactive polymer coating on SS was confirmed using QCM-D in real time on SS sensors by measuring the variation of the resonant frequency (Df) vs. time

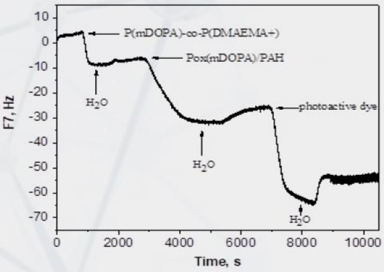


Figure 1. Frequency change upon deposition of P(mDOPA)-co-P(DMAEMA$^+$), Pox(mDOPA)/PAH nanogel and 9-aminoacridine **3** dye measured by QCM-D as a function of time at 25 °C, where the overtone number is 7

Surface and nanomechanical properties of photoactive polymer coating on SS

Atomic force microscopy measurements

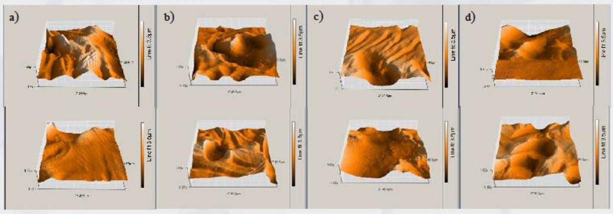


Figure 2. 3D topology of the coatings obtained by AFM: a) pristine SS; b) P(mDOPA)-co-P(DMAEMA+) copolymer; c) P(mDOPA)-co-P(DMAEMA+)/Pox(mDOPA)/PAH; d) P(mDOPA)-co-P(DMAEMA+)/Pox(mDOPA)/PAH/9-aminoacridine 3.

Water contact angle of the photoactive polymer coatings

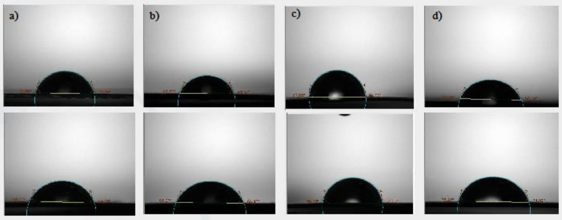


Figure 3. Water contact angle of coatings: a) pristine SS; b) P(mDOPA)-co-P(DMAEMA+) copolymer; c) P(mDOPA)-co-P(DMAEMA+)/Pox(mDOPA)/PAH; d) P(mDOPA)-co-P(DMAEMA+)/Pox(mDOPA)/PAH/9-aminoacridine 3.

Nanoindentation measurement of polymer coatings on SS

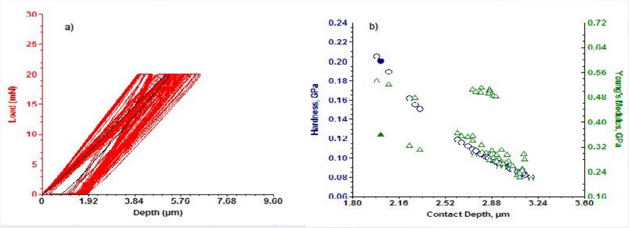


Figure 4. a) Load–displacement curves of 48 nanoindentations and b) Hardness and Young's modulus as a function of contact depth on photoactive polymer nanogel coatings on SS.

Scratch testing of polymer coatings on SS

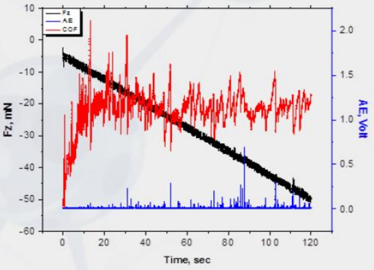


Figure 5. Scratch test of polymer nanogel coatings on SS

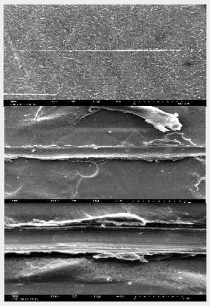


Figure 6. SEM images of polymer coatings on SS

Antibacterial photoactivity of the polymer coatings

Table 1. Antibacterial photoactivity of SS substrate covered by photoactive polymer coatings against *E. coli* ($T_0 = 7{,}1.10^5$ cfu.ml^{-1}; T_0 – initial number of bacteria per ml used for the test).

Sample	1 h of contact		2 h of contact		18 h of contact	
	Survived cells, cfu.ml^{-1}	Reduction rate, %	Survived cells, cfu.ml^{-1}	Reduction rate, %	Survived cells, cfu.ml^{-1}	Reduction rate, %
Photoactive polymer coating	**5,1.10^5**	**28,2**	**8,9.10^4**	**87,4**	**0**	**100**

Conclusions

The results obtained on preparation of photoactive antibacterial polymer coatings showed that the applied technique is successful for the deposition of all layers of the polymer coatings. The QCM-D results demonstrated the deposition of each layer of the polymer coatings, and the water contact angle confirmed the observations. The nanoindentations test showed the coating possess good mechanical properties. The preliminary results of the performed antibacterial photoactivity tests of thus obtained photoactive polymer coatings on SS determined by viable cell-counting method under illumination showed that after 2 hour of contact the reducing rate increase to 87.4% and after 18 hours of contact the reducing rate of 100% was determined. The results showed that thus prepared photoactive polymer coatings could be used as antibacterial coatings on SS.

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Design of PEG-modified magnetic nanoporous silica based miltefosine delivery system

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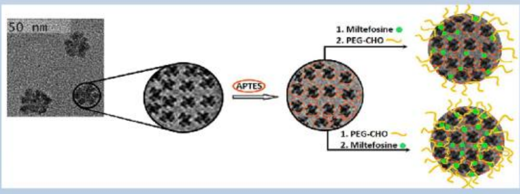
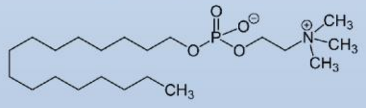
Introduction

In the present study silica nanoparticles incorporating magnetic iron oxides (MS) with sizes around 20 nm were developed. The MS material was modified with NH_2-groups and then grafted by PEG chains. The anticancer drug miltefosine was loaded into the NH_2-modified and PEGylated MS nanoparticles by impregnation procedure resulting in 11-28 % of drug content. PEG chains were also conjugated to the miltefosine loaded MS-NH_2 nanocarrier. The amount of loaded drug and the release properties depend on whether PEGylation of the nanoparticles was performed before or after the drug loading step. The parent and drug loaded samples were characterized by XRD, N_2 physisorption, thermal gravimetric analysis, magnetic measurements, XPS and ATR FT-IR spectroscopy. ATR FT-IR spectroscopic data and DFT calculations supported the interaction between the mesoporous silica surface and miltefosine molecules. The in vitro release profile at pH=7.0 showed sustained drug release and dependence on the experimental design. Free and formulated miltefosine samples were further investigated for antiproliferative activity against malignant HUT-78 cell line. Formulated miltefosine showed superior cytotoxic effect on the tested cells as compared to the free drug. In addition, the MTT assay of the cytotoxic potential of non-loaded silica nanocomposites showed no intrinsic cytotoxicity associated with the carriers.



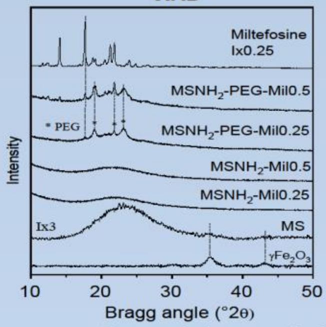
Miltefosine (Mil)



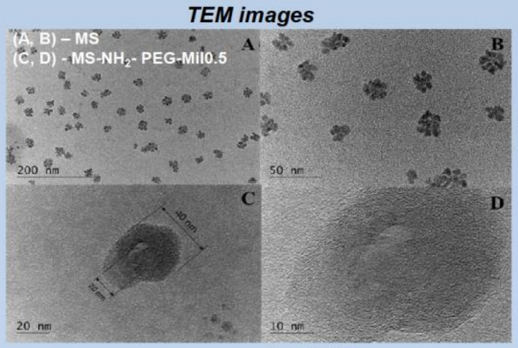
Miltefosine (hexadecyl 2-(trimethylazaniumyl) ethyl phosphate) is an alkylphosphocholine drug with broad activity against various parasite species, cancers, as well as some pathogenic bacteria and fungi.

Characterization

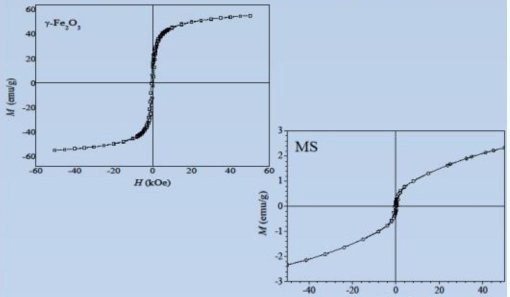
XRD



TEM images



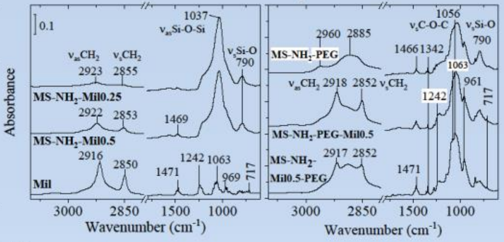
Magnetic properties of iron oxide nanoparticles and MS composite



Textural characteristics

Samples	BET (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)
MS	460	1.26	9.4
MS-NH_2	345	1.20	9.4
MS-NH_2-Mil0.25	295	0.83	9.1
MS-NH_2-Mil0.5	180	0.60	9.0
MS-NH_2-PEG-Mil0.25	45	0.10	-
MS-NH_2-PEG-Mil0.5	36	0.06	-
MS-NH_2-Mil0.25-PEG	78	0.15	-
MS-NH_2-Mil0.5-PEG	65	0.22	-

ATR-FTIR spectra

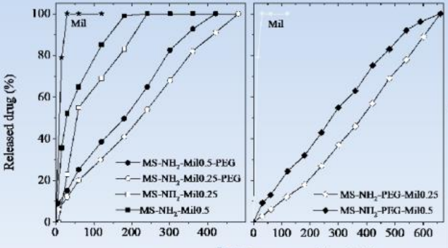


Content of grafted PEG and drug, and loading efficiency

Samples	PEG content[1], wt. %	Drug content[1], wt. %	Drug loading efficiency[2], wt %
MS-NH_2-PEG-Mil0.25	23.2	19.5	78.0
MS-NH_2-PEG-Mil0.5	23.2	27.4	54.8
MS-NH_2-Mil0.25	-	11.4	45.6
MS-NH_2-Mil0.5	-	17.6	35.2
MS-NH_2-Mil0.25-PEG	25.9	11.1	44.4
MS-NH_2-Mil0.5-PEG	24.3	16.3	32.6

[1] Determined by TG analysis, content of NH_2 groups is 7.2 wt.%
[2] Drug loading efficiency=(weight of loaded miltefosin/initial weight of miltefosin)×100

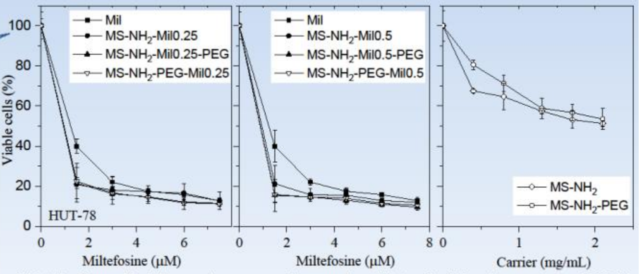
In vitro release at pH=7



In vitro release of the drug was achieved in 2 hours for the M-NH_2-Mil0.5, in about 7 hours for MS-NH_2-Mil0.5-PEG and about 11 hours for MS-NH_2-PEG-Mil0.5

MTT-dye reduction assay

- the encapsulation of miltefosine inside magnetic silica nanoparticles is proven to augment its antineoplastic activity
- miltefosine loading in MS-NH_2 particles led to 22 % lower IC_{50} values in HUT-78(T-lymphocytes) tumor cells, as compared to the free drug
- The entrapment of the drug in PEGylated MS-NH_2 led to additional enhancement of the cytotoxicity, relative to the free drug (app. 30 % lower IC_{50} values)



Cytotoxicity of free and loaded in magnetic-nanoporous silica composites miltefosine after 72 h continuous exposure at 37°C: (a) sample are loaded with 0.25 mg Miltefosine; (b) samples loaded with 0.5 mg drug and (c) non-loaded magnetic silica nanocomposites. Each data point represents the arithmetic mean ± SD of 6 separate experiments.

Conclusions

A composite drug carrier, consisting of magnetic particles incorporated in mesoporous silica and with PEG chains grafted, with sizes around 40 nm was synthesized by a sol-gel method. XRD investigations showed that during the synthesis of the composite, the magnetic nanoparticles were efficiently incorporated into the silica spheres. Magnetic field data evidenced that the magnetic properties of silica composites make them suitable for medical applications. Textural characterizations also proved that miltefosine is localized in the channels of the mesoporous matrix. Loading of miltefosine in amino modified and PEGylated MS nanoparticles resulted in about 11-25% of drug content, mainly being deposited inside the pores of the silica carrier. XRD and FT-IR spectroscopic measurements revealed that by drug loading in amino- and PEGylated magnetic silica, more effective formulations were obtained. Spectroscopic data suggest weak bonding between the surface of the mesoporous silica nanoparticles and miltefosine molecules. *In vitro* release process at pH=7 showed sustained effect, reaching total drug release within 11 h for the miltefosine loaded PEGylated MS systems. The formulations of miltefosine based on the PEGylated magnetic silica nanoparticles were evaluated *vs.* free drug for antiproliferative activity against human tumor cell line, and proved to exert superior antineoplastic potential. In conclusion, the obtained results proved the designed composite material to be an appropriate nanocarrier of miltefosine, but also demonstrating advantageous features of a platform for delivery of a broad range of drugs.

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10. 09. 2020 г., Институт по полимери - БАН

Synthesis and photocatalytic investigations of macrocyclic oligomer/polystyrene/TiO_2/CeO_2 composite

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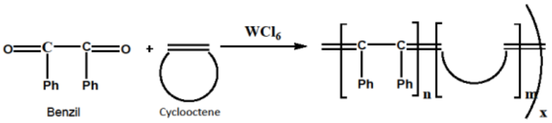
AIM

- Synthesis of segmental oligomer via copolymerization of conjugated dicarbonyl compounds and cyclooctene, using compounds of the transition metals (WCl_6) as catalyst.
- Preparation of segmental oligomer/polystyrene/TiO_2/CeO_2 hybrid nanocomposite.
- Characterization of prepared hybrid nanocomposite using PXRD analysis and FTIR spectroscopy.
- Photocatalytic investigations of the prepared hybrid nanocomposite in the reaction of degradation of Reactive Black 5 dye under UV light.

SYNTHESIS

I.



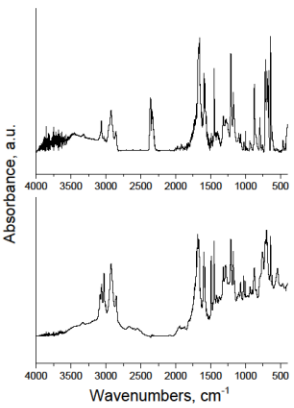
Experimental conditions:
Benzil : cyclooctene : WCl_6 = 1:1:1
Solvent-Chlorobenzene
Temperature: 90˚C, Time: 3h.

II. The commercial powders of TiO_2 and CeO_2 (Alfa Aesar GmbH & Co KG) were mechanochemically treated in an agate milling container of 80 ml volume using a Highenergy planetary ball mill type PM 100, Retsch, Germany. The process was performed at milling speed – 400 rpm, milling time interval of 10 minutes and mass ratio of powder to balls 1:9 in air media. Then the mechanochemically treated TiO_2 and CeO_2 were mixed in weight ratio 1:1.

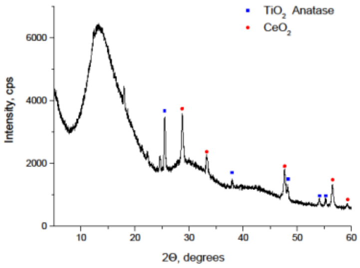
III. The composite was prepared by sol–gel method. The synthesized oligomer was dissolved in $CHCl_3$ and added TiO_2/CeO_2. After that the solution of polystyrene in CH_2Cl_2 was mixing with segmental oligomer/TiO_2/CeO_2 for 1hour at room temperature. A gel form was obtained, which is dried on 30˚C.

RESULTS

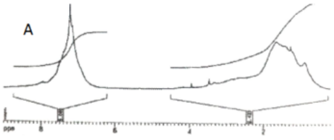
Characterization



FTIR spectra of A) copolymer of benzil and cyclooctene; B) segmental oligomer/polystyrene/TiO_2/CeO_2 hybrid nanocomposite.



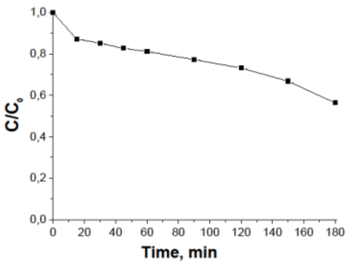
PXRD pattern of prepared segmental oligomer/polystyrene/TiO_2/CeO_2 hybrid nanocomposite.



^1H NMR spectrum of A) copolymer of benzil and cyclooctene.

Photocatalytic investigations

The photocatalytic efficiency of synthesized hybrid nanocomposite was tested for degradation of Reactive Black 5 (RB5) dye as model contaminant in aqueous solution (5 ppm) under UV-light.



The concentration ratio C/C_0 of the RB5 dye in aqueous solution with time under UV irradiation using prepared hybrid nanocomposite as photocatalyst.

CONCLUSIONS

- ☐ Segmental oligomer (M=819 g/mol) has been synthesized via copolymerization of conjugated dicarbonyl compounds and cyclooctene, catalyzed by WCl_6.
- ☐ The segmental oligomer/polystyrene/TiO_2/CeO_2 hybrid nanocomposite has been successfully prepared.
- ☐ The prepared hybrid nanocomposite demonstrates photocatalytic ability for degradation of RB5 dye under UV light.

Организационен екип

Председател

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