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7-ма Рамкова програма.

Списък на участниците:

Постер № 1. Elena Drakalska, Denitsa Momekova, Stergios Pispas, Nikolay Lambov, Stanislav Rangelov;

Steric stabilization of liposomes by copolymers with different composition

Медицински Университет - София, Фармацевтичен факултет

Постер № 2. Ekaterina Stoyanova, Irina Karadjova, Methody Karadjov, Neli Koseva;

Analytical Methods for Characterization of Polymeric System for Cisplatin Delivery;

СУ «Св. Климент Охридски», Факултет по Химия и Фармация

Постер № 3. Х. Грънчарова, П. Шестакова, Е. Василева;

Изследване на свойствата на хидрогелове на полисулфобетаин в зависимост от концентрацията на NaCl;

СУ «Св. Климент Охридски», Факултет по химия и фармация

Постер № 4. М. Симеонов, Д. Рабаджиева, С. Тепавичарова, А. А. Апостолов, Е. Василева; *Хибридни органично-неорганични материали на базата на взаимнопроникващи полимерни мрежи поли(акрилова киселина)□полиакриламид и калциев хидроксилапатит*;

Софийски университет «Св. Климент Охридски», Факултет по химия и фармация

Постер № 5. Павлина Петрова, Стоян Милошев, Христо Новаков;

Сулфонатоалкилирани каликс□4□резорцинаренови структури - гостоприемни домакини за σ-амино-р-хидроксибензил пеницилинови молекули;

Химико-технологичен и Металургичен Университет - София

Постер № 6. R. Bryaskova, Z. Todorova, N. Lazarova, N. Georgieva, R. Tzoneva;

Cell adhesive behavior of PVA-based hybrid materials with silver nanoparticles and removal of chromium ions from water;

Химико-технологичен и Металургичен Университет - София

Постер № 7. Иванка Петрова, Петър Тодоров, Юлий Цеков, В. Ангелов, И. Боровански, Е. Иванов, Р. Коцилкова;

Микромеханични и трибологични изследвания на PP□MWCNTs нанокомпозити;

Институт по механика - БАН

Постер № 8. Вериславъ Ангелов, Юлий Цеков, Румяна Коцилкова;

Структурно охарактеризиране на дву- и трифазни нанокомпозити получени на базата на епоксидна смола;

Институт по механика - БАН

Постер № 9. Анита Богомилова, Нели Косева, Кольо Троев;

Novel Multifunctional Polyphosphoesters;

Институт по полимери - БАН

Постер № 10. Е. Халаджова, С. Халачева, Ст. Рангелов, В. Пашева;

Gene delivery systems based on novel comb-like PEI polymers;

Институт по полимери- БАН

Постер № 11. Елена Корина, Оля Стоилова, Невена Манолова, Илия Рашков;

Дизайн и потенциални приложения на хибриден наноструктуриран нетъкан текстил, съдържащ титанов диоксид;

Институт по полимери - БАН

Постер № 12. Ivanka Kraicheva, Elitsa Vodenicharova, Anita Bogomilova, Ivelina Tsacheva, Kolio Troev;

Poly(oxyethylene aminophosphonates)s synthesis, NMR characterization and biological evaluation;

Институт по полимери - БАН

Постер № 13. Emilya D. Ivanova, Nadya I. Ivanova, Margarita D. Apostolova, Sevdalina C. Turmanova, Ivaylo V. Dimitrov;

Polymer gene delivery vectors encapsulated in thermally sensitive bioreducible shell;

Институт по полимери - БАН

Постер № 14. Filip Ublekov, Hristo Penchev, Maya Staneva, Vassil Georgiev, Ivan Radev, Vesselin Sinigersky;

Nanostructured polymer electrolyte membranes for fuel cells;

Институт по полимери - БАН

Постер № 15. Георги Л. Георгиев, Петър Петров, Симона Димчевска, Катерина Горачинова; *Лекарство-доставящи системи на основата на поли(акрилова киселина)-поли(ε-капролактон)-поли(акрилова киселина) триблокови съполимери;*

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Постер № 16. Гюлджан Якуб, Антония Тончева, Невена Манолова, Илия Рашков;

Микровлакнести материали от полимлечна киселина и куркумин, получени чрез електроовлакняване;

Институт по полимери - БАН

Постер № 17. Калин Калинов, Милена Игнатова, Вера Максимова, Илия Рашков, Невена Манолова;

Антибактериални материали от електроовлакнен поликапролактон, модифициран с полиелектролитен комплекс полиакрилова киселина – N,N,N-триметилхитозан йодид;

Институт по полимери - БАН

Постер № 18. Мария Кънчева, Антония Тончева, Илия Рашков, Невена Манолова;

Получаване и охарактеризиране на нановлакна от полиакрилонитрил с включени наночастици от ZnO чрез електроовлакняване;

Институт по полимери - БАН

Постер № 19. Maya Staneva, Christo Penchev, Filip Ublekov, Vesselin Sinigersky, Elefteria Lefterova; *Polymer Electrolyte Membranes for Fuel Cells – PBI containing immobilised sulphonic acid groups*;

Институт по полимери – БАН

Постер № 20. Nikoleta Stoyanova, Rosica Mincheva, Dilyana Paneva, Nevena Manolova, Philippe Dubois, Iliya Rashkov;

Novel microfibrous materials based on polylactide and poly(butylene succinate) prepared by electrospinning;

Институт по полимери - БАН

Постер № 21. Павел Бакърджиев, Станислав Рангелов, Деница Момекова;

Стерично стабилизиране на липозоми чрез новосинтезирани полимери на основата на полиглицидол, конюгиран с липидо-подобна котва;

Институт по полимери-БАН

Постер № 22. Radostina Kalinova, Chinh Ngo, Elise Hennebert, Rosica Mincheva, Philippe Leclére, Patrick Flammang, Roberto Lazzaroni, Philippe Dubois;

Surface modification of silicon coatings with amphiphilic block copolymers and study of their adhesion properties;

Институт по полимери - БАН

Постер № 23. Silvia Dimova, Katerina Zaharieva, Christo Jossifov, Zara Cherkezova-Zheleva, Boris Kunev;

What is the effect of catalysts for metathesis and other transformation?;

Институт по полимери – БАН & Институт по катализ – БАН

Постер № 24. Веселина Стойнева, Петър Петров;

pH-чувствителни супер-макропорести криогелове на основата на фотоомрежени хитозан и хидроксиетилцелулоза;

Институт по полимери – БАН

Постер № 25. Petar D. Petrov, Krassimira Yoncheva, Pavlina Mokreva, Yana Peneva-Stoyanova, Spiro Konstantinov, Juan M. Irache, Axel H.E. Müller;

Synthesis and aqueous solution properties of PEO-PnBA and PEO-PnBA-PAA block copolymers;

Институт по полимери - БАН

Постер № 26. G. Nikolova, D. Ivanova, B. Grigorov, E. Georgieva, Y. Karamalakova, A. Zheleva, V. Gadjeva;

The influence of lipid- and water-soluble antioxidants on toxic oxidative effects of madopar in experimental mice models – EPR study;

Тракийски Университет - Стара Загора, Медицински Факултет

Постер № 27. Y. Karamalakova, G. Nikolova, R. Kumar, R. Arora, R. K. Sharma, E. Georgieva, A. Zheleva, V. Gadjeva;

Biodistribution of synthetic and natural antioxidants in organs of experimental mice: comparative epr investigation

Тракийски Университет - Стара Загора, Медицински Факултет

Постер № 28. Tarek Salem, Dieter Pleul, Frank Simon;

Plasma-based surface functionalization of polyester□wool fabric and its interaction with acid dyes;

National Researcher Centre, Cairo, Egypt

ПОСТЕР № 1

STERIC STABILIZATION OF LIPOSOMES BY COPOLYMERS OF DIFFERENT COMPOSITION

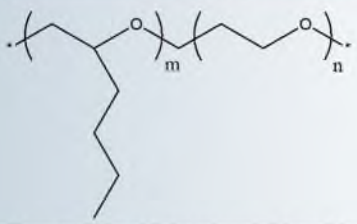
Elena Drakalska*[a], Denitsa Momekova[a], Stergios Pispas[b], Nikolay Lambov[a], Stanislav Rangelov[c]

[a]Faculty of Pharmacy, Medical University of Sofia, 2 Dunav Str., 1000 Sofia, Bulgaria, [b]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation 48 Vass. Constantinou Ave.11635 Athens, Greece, [c]Institut of Polymers, Bulgarian Academy of Sciences, *corresponding author: edrakalska@yahoo.com

INTRODUCTION: Liposomes have been considered as almost universal carriers for drugs and diagnostic agents, as they are biodegradable, non toxic and able to accommodate both hydrophilic and hydrophobic agents. A major hurdle towards *in vivo* utilization of liposomes is their prompt sequestration by the cells of the RES. Typically, prolonged circulation of the liposomes is achieved using poly(ethylene glycol) (PEG) covalently connected to a lipid residue which is incorporated into the liposome bilayer. The polymer chains create a repulsive barrier around liposomes, which reduces the interactions with blood components and consequently increases the blood circulation time. At a certain critical content referred to as saturation limit, which depends on lipid composition and PEG molecular weight, the PEG-lipids induce a transition from bilayers to a micellar phase.

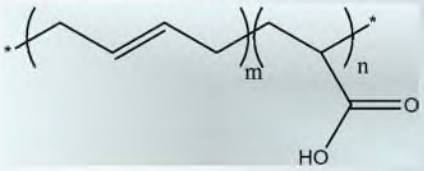
AIM: In this study we investigate the effects of the novel copolymers on the morphological properties and membrane integrity of lipid bilayers based on dipalmitoylphosphathidylcholine:cholesterol and pH-sensitive liposomes based on dioleoylphosphathidyl ethanol amine:cholestherylhemisuccinate liposomes. The copolymers were selected to differ in the type and degree of polymerization of both the hydrophilic and hydrophobic chains. The chemical structures, composition and molecular weight of the copolymers are given in Figure 1. To meet this objective we used dynamic light scattering, cryo-transmission electron microscopy and fluorescence spectroscopy.

Poly(hexene oxide)-b-poly(ethylene oxide)



$EOHO_{206}$ M_w =14 000; PEO content 83 mol %
$EOHO_{208}$ M_w =7 800; PEO content 64 mol %

Polyisoprene-b-poly(acrylic acid)



PI-PAA
Mw = 12 000; PI content 36 mol %

RESULTS AND DISCUSSION: The utilized method for preparation of liposomes is knwon to yield uniform, unilamelar vesicles with mean diameter of about 140 nm. The apparent particle diameters were found to slightly depend on the polymer/phospholipid ration and the copolymer composition. Within all copolymer to phospholipid ratios studied, the size distributions were monomodal with a dispersity index typically below 0.2 (Fig. 2).

The liposome morphology was investigated by cryo-TEM. Within the series of liposomes stabilized with the non-ionic $EOHO_{208}$ and $EOHO_{206}$ copolymers in all micrographs the predominant objects were intact, well separated and unilamellar liposomes. The first signs for liposomal destabilization (liposomal openings, bilayer fragments or discks) were observed at copolymer concentrations as high as 7.5 mol %. The fraction of disks observed at 7.5 mol % was higher for the copolymer $EOHO_{208}$. Within the serias of liposomes stabilized with pH-sensitive polymer PI-PAA the predominant objects in all images were liposomes, however, a micellar fraction was found to co-exist with well separated and intact liposomes at copolymer concentration 5 mol % (Fig. 3).

A leakage assay using calcein was carried out in order to evaluate the membrane permeability of non pH-sensitive DPPC:CHOL and pH-sensitive DOPE:CHEMs liposomes stabilized with increasing amounts (2.5 – 7.5 mol%) of copolymer PI-PAA as a function of pH.The results obtained show that PI-PAA can induce pH-dependent calcein release from DPPC liposomes at low pH 4.5 and at the same time the tested polymer did not compromise the pH-sensitivity of DOPE liposomes (Fig. 4).

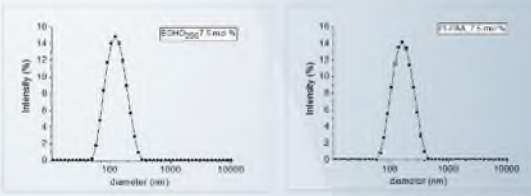


Figure 2. Size distribution of liposomes stabilized with 7.5 mol % of copolymers $EOHO_{208}$ (left) and PI-PAA (right)

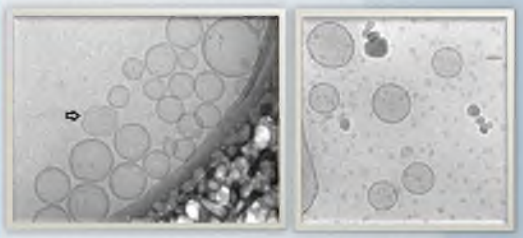


Figure 3. Cryo-TEM images of DPPC:Chol liposomes stabilizied with 7.5 mol % $EOHO_{206}$ (left) and 7.5 mol % PI-PAA (right). The arrow show liposomal opening (left) and micelles (right).

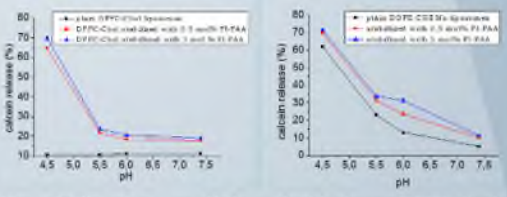


Figure 4. Spontaneous pH-dependent leakage at 37 C of calcein from DPPC:CHOL (left) and DOPE:CHEMs (right) liposomes Plain (squares) or stabilized with 2,5 (circles) or 5 mol% (triangles) PI-PAA.

CONCLUSIONS: This study shows that the utilized block copolymers can be considered as promising sterically stabilizing agents for the development of long circulating liposomes. An important advantage of the copolymer PI-PAA is that incorporation in the DOPE:CHEMs membrane does not deteriorate the pH-sensitivity of the formulation and, even more, the acid-triggered calcein leakage was optimized. In addition, this polymer can induced pH-dependant release from non pH-sensitive DPPC liposomes which make this polymer promissing candidate for preparation of a second generation pH-sensitive liposomes.

ACKNOWLEDGEMENTS: The present study received financial support from the National Science Fund (Grand ДФНИ-501/25 and DCVP 02/2)

ПОСТЕР № 2

Analytical Methods for Characterization of Polymeric System for Cisplatin Delivery

Ekaterina Stoyanova[1,3*], Irina Karadjova[1], Methody Karadjov[2], Neli Koseva[3]

[1]Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski", 1 James Bourchier Blvd, 1164 Sofia, Bulgaria;
[2]Geological Institute, Bulgarian Academy of Sciences, Acad. Georgi Bonchev Str. Bl.24, 1113 Sofia, Bulgaria
[3]Institute of Polymers, Bulgarian Academy of Sciences, Acad. Georgi Bonchev Str. Bl.103, 1113 Sofia, Bulgaria
*E-mail:ajfa_jest@abv.bg

Cis-Dichlorodiamminoplatinum(II) (cisplatin) was immobilized in a star-shaped polymer carrier consisting of a hyperbranched polystyrene core and arms made up from polyacrylic acid. In order to define whether this polymer can be used as a drug delivery system for cisplatin, its characteristics, e.g. loading efficiency and release profile of cisplatin from the polymer in phosphate buffered saline (PBS), have to be assessed, and hence an appropriate analytical procedure for precise and reliable determination of Pt(II) has to be established. Optimal instrumental parameters for Pt measurement by common used atomic spectrometric methods ETAAS and ICP-OES in various examined media were defined. Matrix interferences observed, related to both techniques were evaluated, and possibilities were compared and critically discussed.

Synthesis of the star polymer

Star polymers assigned as PScorePAarm were obtained through acidic hydrolysis of the linear poly(*tert*-butyl acrylate) arms of the precursors to polyacids thus yielding polymers with branched hydrophobic interior and hydrophilic multifunctional shell from poly(acrylic acid) chains.

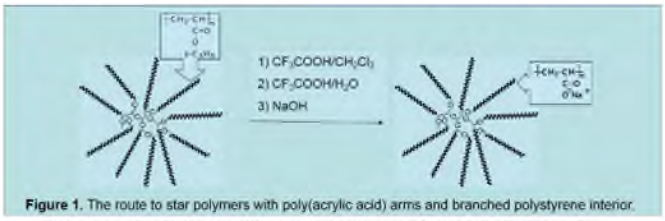


Figure 1. The route to star polymers with poly(acrylic acid) arms and branched polystyrene interior.

Release of platinum(II) complexes in physiological saline

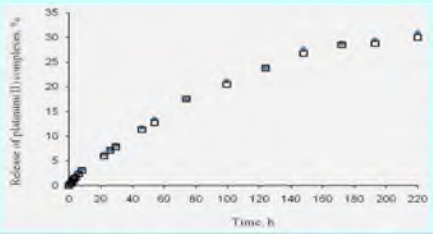


Figure 3. Release of Pt(II) complexes from cisplatin-loaded star copolymers in phosphate buffered saline (pH 7.4, 0.14 M NaCl) at 37 °C: (◆) $PS_{core}PA_{arm}58$ -Pt and (□) $PS_{core}PA_{arm}38$-Pt.

Loading of the polymer carrier with cisplatin

Table 1.
Data about the star copolymer loading with cisplatin in an aqueous solution at a drug concentration of 2 mg/ml temperature 22°C, pH 8 and incubation time 24 hours

Sample	Feeding molar ratio [carboxylate] [cisplatin]	Loading efficiency %	Drug mass fraction in the loaded particles %
$PS_{core}PA_{arm}38$	3	80	45
$PS_{core}PA_{arm}58$	3	84	46

Figure 2. Schematic presentation of the possible ways of cisplatin binding to the star polymers.

Analytical methods for Pt determination

Analytical procedure based on ETAAS

The ETAAS-measurements were carried out on a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer (Fig. 4).

Figure 4. Perkin-Elmer Zeeman spectrometer

The method of ETAAS was used for evaluation of cisplatin release profile from polymer molecules Experiments showed that loss free pyrolysis temperature of 1300°C could be achieved, nevertheless even hold time of 60s at this temperature could not completely eliminate strong and irreproducible background absorption signal observed, evidently due to NaCl presented in PBS. The only possibility is injection of smaller sample volumes or at least twofold PBS sample dilution with doubly distilled water. Atomization curves presented in Fig. 5 also showed strong signal depression for undiluted samples. Almost highest possible atomization temperature of 2650°C should be used for complete Pt atomization in PBS solution.

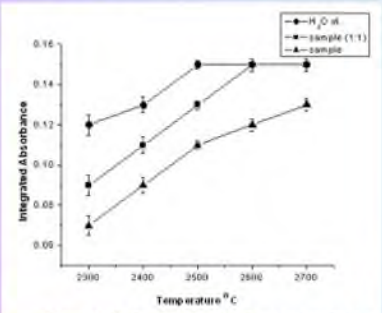


Figure 5. Pt atomization curves for aqueous standard solution, sample and twofold diluted sample.

Analytical procedure based on ICP-OES

The ICP-OES-measurements were carried out on a ULTIMA 2, Jobin Yvon spectrometer Fig. 6). The technique of ICP-OES was applied for assessment of the loading efficiency of the star macromolecule – a procedure that requires measurement of Pt in the presence of polymer matrix. The method was used for evaluation of cisplatin release profile from the polymer carrier as well. Results obtained for the ratio of the slopes of calibration graphs in the presence of polymer matrix (b_s) and for aqueous standards (b_{aq}) undoubtedly showed absence of any spectral and matrix interferences. Simple calibration against aqueous standard calibration graph is recommended for Pt quantification.

Table 2. Comparative results for Pt content (mg L^{-1}) in PBS by ETAAS and ICP-OES (three parallel determinations.

Sample	ETAAS [mean±s]	ICP-OES [mean±s]
Sample 1	0.07±0.01	0.06±0.01
Sample 2	0.28±0.02	0.26±0.02
Sample 3	0.74±0.05	0.75±0.04

While performing measurements of Pt at low concentration levels in PBS, it might be expected that the large amount of Na-salts can cause spectral and ionization interferences. In order to avoid additional use of ionization buffers, calibration against calibration curve prepared with matrix matched standards based on PBS buffer is recommended. As far as certified reference materials are not available, the accuracy of both recommended procedures for Pt determination in PBS e.g. by using ETAAS or ICP-OES was approved by analysis of parallel samples under defined optimal instrumental parameters. The results presented in Table 2 show a very good agreement achieved that confirms validity and versatility of analytical methods developed for Pt determination in PBS.

Figure 6. ULTIMA Jobin Yvon spectrometer

Analytical application

The developed analytical procedures allowed determination of two key characteristics of the delivery systems, i.e. the loading efficiency and the release profile. Loading efficiency is defined as the amount of the loaded drug against the one added to the reaction mixture. Pt determination showed high loading efficiency for the star polymer - 82% The percentage of Pt(II) released from the macromolecular carrier was about 30%. The observed sustained release of Pt(II) complexes from the carrier has a great advantage for the passive drug targeting to solid tumors.

Conclusions

Both atomic spectrometric methods, ETAAS and ICP-OES, are appropriate for characterization of investigated new polymeric delivery system for cisplatin. Accurate and precise results could be obtained after careful optimization of instrumental parameters. Calibration against matrix matched standards is recommended in both cases. Analytical method developed based on ICP-OES measurements is more suitable for routine laboratory practice taking into account lower detection limits achieved in PBS and longer linear working range.

Acknowledgement
The support by the POLINNOVA project (GA 316086) is highly acknowledged

ПОСТЕР № 3

ИЗСЛЕДВАНЕ НА СВОЙСТВАТА НА ХИДРОГЕЛОВЕ НА ПОЛИСУЛФОБЕТАИН В ЗАВИСИМОСТ ОТ КОНЦЕНТРАЦИЯТА НА NaCl

Х. Грънчарова[1,2], П. Шестакова[2], Е. Василева[1]

[1]Лаборатория по структура и свойства на полимерите, бул. „Джеймс Баучер" No 1, Факултет по химия и фармация, СУ"Св. Кл. Охридски", 1164 София, България; email: hgtina@abv.bg

[2]Лаборатория по ЯМР, Институт по органична химия с Център по фитохимия, ул. „Акад. Георги Бончев", бл. 9, Българска академия на науките, 1113 София, България.

I.Въведение

Интересът към полибетаините нараства все повече в последните години, главно поради изключително добрите им кръво- и биосъвместимост. Известно е, течностите в човешкия организъм са солеви разтвори, а добрите кръво- и биосъвместимост се проявяват именно там.

II. Цел

Целта на настоящето изследване бе да се изследва взаимодействието между солеви разтвор и мрежи на поли(3-диметил (метакрилоилоксиетил) амониев пропансулфонат) (ПСБ) (Схема 1), което лежи в основата на добрата биосъвместимост на полибетаините.

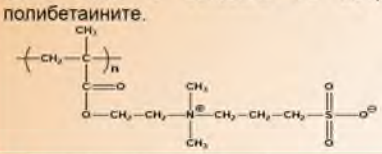


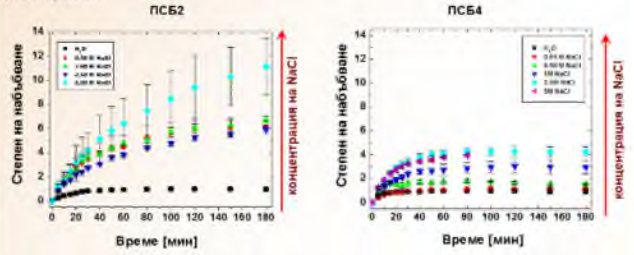
Схема 1. Поли(3-диметил (метакрилоилоксиетил) амониев пропансулфонат) (ПСБ)

III. Експериментална част

Синтез на мрежи на ПСБ: Към 1М N,N-диметил (метакрилоилоксиетил) амониев пропансулфонат се прибавя калиев персулфат (КП) (0.1мол.%) и омрежващ агент N,N' метилен-бис-акриламид (МБАА) с концентрации 2 тегл.% и 4 тегл.%. По този начин бяха получени две полимерни мрежи с различна гъстота, съответно ПСБ2 и ПСБ4. Проведена бе омрежваща полимеризация, при 60°C за 6 часа.

IV. Резултати

С нарастване концентрацията на NaCl се наблюдава т. нар. антиполиелектролитен ефект, т.е. увеличава се степента на набъбване на двете мрежи ПСБ2 и ПСБ4. По-рехавата мрежа, ПСБ2, набъбва в по-голяма степен в сравнение с ПСБ4. Кинетичните криви показват начален етап на бързо набъбване, последван от етап на насищане.

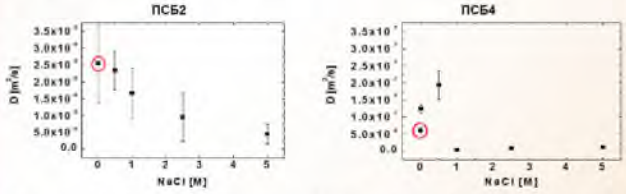


Фигура 1. Кинетика на набъбване на ПСБ2 и ПСБ4 във вода и водни разтвори на NaCl.

Схема 2. Дипол-диполни клъстери в ПСБ и тяхното разрушаване при прибавяне на NaCl.

G. Georgiev, et. al., *Biomacromolecules* 2006, 7, 1329-1334.

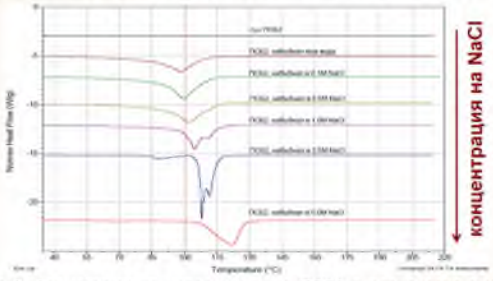
Добавянето на NaCl води до разрушаване на дипол-диполните клъстери, образуващи се в ПСБ (Схема 2), което води до нарастване на степента на набъбване на ПСБ.



Фигура 2. Зависимост на дифузионния коефициент *D* на разтворителя от концентрацията на NaCl при дифузия на вода и водни разтвори на NaCl в ПСБ2 и ПСБ4

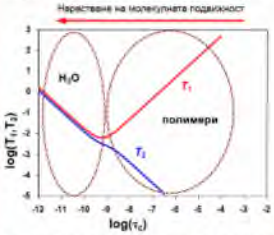
Дифузионният коефициент на разтворителя в ПСБ2 и ПСБ4 намалява с нарастване на концентрацията на NaCl, поради нарастващото взаимодействие ПСБ-разтворител.

Нарастването на взаимодействието ПСБ-вода води до увеличаване на количеството свързана вода в получените хидрогелове. Това увеличаване на количеството свързана вода бе регистрирано с ДСК.



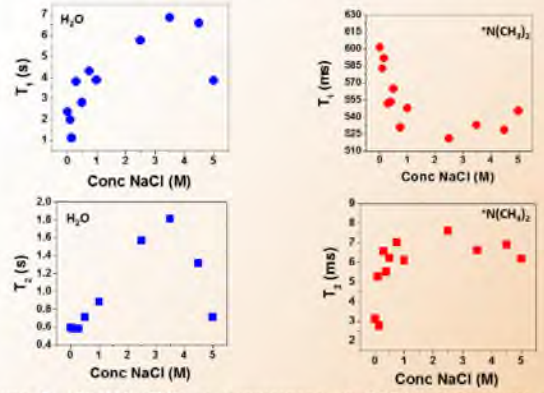
Фигура 3. Термограми на хидрогелове на ПСБ2 в равновесната им степен на набъбване във вода водни разтвори на NaCl

Охарактеризиране на хидрогеловете на ПСБ с HR-MAS ЯМР



Фигура 4. Теоретична зависимост на T_1 и T_2 от молекулната подвижност, изразена чрез корелационното време τ_c

T_1 е чувствително към взаимодействие на молекулните фрагменти с тяхното обкръжение, докато T_2 зависи от локалната фрагментна подвижност. За малки молекули (H_2O) важи зависимостта наляво от минимума, а за макромолекули (полимери) – надясно от минимума.



Фигура 5. HR-MAS ЯМР на хидрогелове на ПСБ4 - независимо измерени времена на релаксация T_1 и T_2

Изследванията с HRMAS NMR показват, че с увеличаване концентрацията на NaCl, нараства подвижността на водните молекули и на полимерните вериги, като минава през максимум.

V. Изводи:

- ❑ Дифузията на вода и водни разтвори на NaCl в полисулфобетаинова мрежа е аномална, независимо от гъстотата на мрежата и концентрацията на NaCl.
- ❑ Изследванията с DSC показват, че в хидрогеловете на ПСБ във вода и ниски концентрации NaCl преобладава несвързана вода. С увеличаване на концентрацията на NaCl, нараства съдържанието на свързана вода.
- ❑ Резултатите от ЯМР с въртене под магически ъгъл (HR-MAS ЯМР) потвърждават изводите от динамичното набъбване и ДСК, като показват, че с увеличаване на концентрацията на NaCl, нараства подвижността на водните молекули и на полимерните вериги, минавайки през максимум. Тези промени на свойствата на хидрогеловете на ПСБ се дължат на разрушаването на тяхната специфична структура, поради екраниращото действие на йоните на солта.

Благодарности: Тази работа е финансирана от Фонд "Научни изследвания", Проект ДРНФ 02/13 15.12.2009.

ПОСТЕР № 4

ХИБРИДНИ ОРГАНИЧНО-НЕОРГАНИЧНИ МАТЕРИАЛИ НА БАЗАТА НА ВЗАИМНОПРОНИКВАЩИ ПОЛИМЕРНИ МРЕЖИ НА ПОЛИ(АКРИЛОВА КИСЕЛИНА) (ПАК) И ПОЛИАКРИЛАМИД (ПААМ) И КАЛЦИЕВ ХИДРОКСИЛАПАТИТ

М. Симеонов[1], Д. Рабаджиева[2], С. Тепавичарова[2], А. А. Апостолов[1], Е. Василева[1]

[1] *Лаборатория по структура и свойства на полимерните материали, Факултет по химия и фармация, Софийски Университет.*
[2] *Институт по обща и неорганична химия, Българска академия на науките.*

ВЪВЕДЕНИЕ

Взаимнопроникващите полимерни мрежи (ВПМ) представляват комбинация от две или повече полимерни мрежи, които се преплитат една в друга без да образуват ковалентни връзки помежду си. ВПМ са фазово-разделени структури, притежаващи способността да абсорбират енергия. Ето защо те притежават много добри механични, вибрационно-поглъщащи и звукоизолаторни свойства.

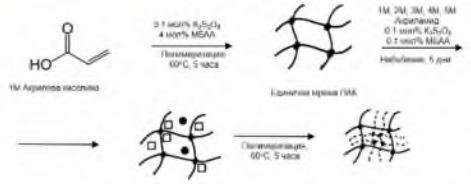
Биоминерализацията е процеса, чрез който се формират костите, зъбите, черупките и т.н. в живите организми. Този процес се контролира и подпомага от белтъци, съдържащи отрицателни заряди (костен сиалопротеин, остеокалцин и др.), които служат като центрове, координиращи Ca^{2+} йони, от които започва процеса на костен растеж.

ЦЕЛ

Целта на настоящото изследване е като се имитира естествения процес на формиране на костите да се използва фазово разделента структура на ВПМ на ПАК и ПААМ като матрица за *in situ* кристализация на калциеви фосфати, като ПАК играе ролята като аналог на сиалопротеините.

Синтез на ВПМ на ПАК и ПААМ

Получаване на взаимнопроникващи полимерни мрежи ПАК/ПААМ и ПААМ/ПАК



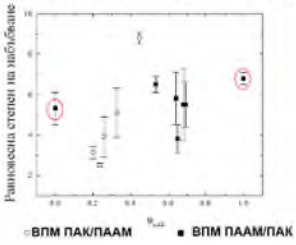
*по аналогичен начин, чрез промяна на последователността се синтезира единичната мрежа ПААМ и ВПМ ПААМ/ПАК

Състав на получените ВПМ

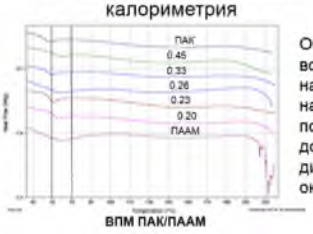
	$\Phi_{ПАК}$
ПААМ	0
ВПМ ПАК/ПААМ	0.20
	0.23
	0.26
	0.33
	0.45
ВПМ ПААМ/ПАК	0.53
	0.64
	0.65
	0.68
	0.69
ПАК	1

Охарактеризиране на ВПМ ПАК/ПААМ и ВПМ ПААМ/ПАК

Равновесна степен на набъбване

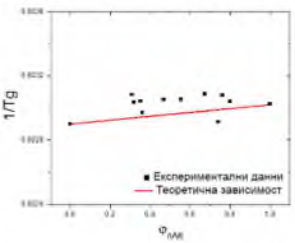


Диференциална сканираща калориметрия



Общият преход на встъкляване на ВПМ, намиращ се между T_g на единичните мрежи, показва размер на домените на дисперсната фаза около 10-20нм.

Уравнение на Фокс за двукомпоненти полимерни системи

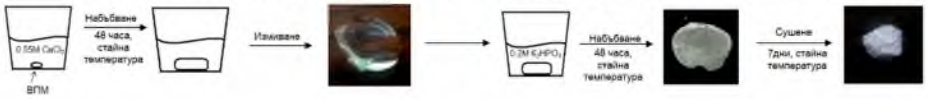


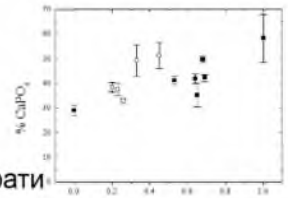
$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{1-x_1}{T_{g,2}}$$

T.G. Fox, Bull. Am. Phys. Soc. 1 (1956) 123.

Отклонението от уравнението на Фокс вероятно се дължи на значителната междуфазова повърхност между ПАК и ПААМ.

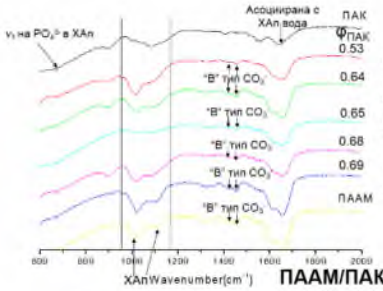
In situ утаяване и охарактеризиране на калциеви фосфати във ВПМ ПАК/ПААМ и ПААМ/ПАК



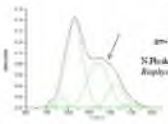


Охарактеризиране на хибридните материали от ВПМ и калциеви фосфати

Инфрачервена спектроскопия



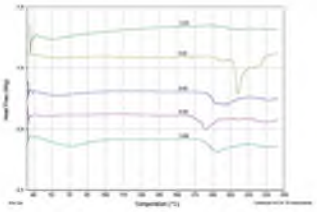
Получава се карбонатен ХАп "тип B" (B-тип" $CO_3^{2-} \leftrightarrow PO_4^{3-}$), преобладаващ в костите на млади индивиди.



$$Y = aX^b + c$$

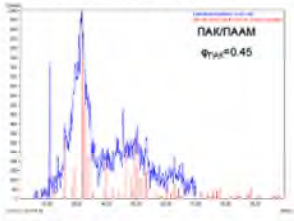
Определяне на размера на кристалитите на ХАп посредством деконволюция на характеристичната ивица от ИЧ спектъра отговаряща на трептенето на връзката P-O.

Диференциална сканираща калориметрия (ДСК)

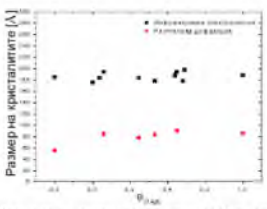


Модулирана ДСК на ВПМ ПААМ/ПАК с отложени калциеви фосфати

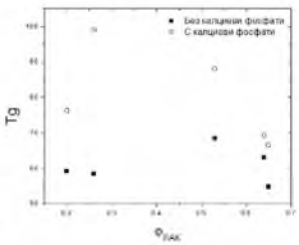
Рентгеноструктурен анализ (РСА)



Рефлексите в рентгенограмите на ВПМ с отложен калциев фосфат потвърждават образуването на ХАп. Дифрактограмите са използвани за оценка на размера на получените кристалите от ХАп



Размерът на кристалитите на ХАп, отложен във ВПМ на ПАК и ПААМ, оценен от ИЧ спектрите е около 180 Å. За същите кристалити РСА дава размер около 80 Å.



Наличието на калциев фосфат във ВПМ води до повишаване на Tg, което показва образуването на нанокомпозитна структура.

Изводи:

1. За ВПМ на ПААМ и ПАК е наблюдавана една обща температура на встъкляване, намираща се между температурите на встъкляване на двата компонента ПАК и ПААМ. Това означава, че получената ВПМ има фазово разделена структура с размер на домените 10-20 nm.
2. За първи път ВПМ на ПААМ и ПАК бяха приложени като матрици за биомиметична кристализация на калциеви фосфати.
3. Наблюдаваното повишаване на температурата на встъкляване на полимерната матрица доказва взаимодействие между ВПМ и отложените в тях калциеви фосфати, т.е. получаването на хибридни органично-неорганични материали.
4. Съставът на ВПМ ПААМ/ПАК и ПАК/ПААМ може да бъде използван за контрол на количеството отложени калциеви фосфати, като ролята на ПАК в този процес е определяща.

Благодарности: Тази работа е финансирана от Министерството на образованието по проект **"BONEIMPLANTS" DTK 02-70/2009**.

ПОСТЕР № 5

СУЛФОНАТОАЛКИЛИРАНИ КАЛИКС[4]РЕЗОРЦИНАРЕНОВИ СТРУКТУРИ – ГОСТОПРИЕМНИ ДОМАКИНИ НА α-АМИНО-р-ХИДРОКСИБЕНЗИЛ-ПЕНИЦИЛИНОВИ МОЛЕКУЛИ

Павлина Петрова [1], ***Стоян Милошев*** [1] , ***Христо Новаков*** [2]

[1] *Химикотехнологичен и Металургичен Университет, катедра „Полимерно инженерство", бул. „Кл.Охридски" 8, 1756 София*
[2] *Институт по полимери, БАН, ул. акад. Г. Бончев 103А, 1113 София*

Въведение

Каликсаренните са съединения притежаващи специфични и уникални свойства, което определя растящият интерес към тяхната разнообразна употреба. Резорцинаренните могат лесно да се функционализират и получените производни да се използват като градивни елементи за получаването на различни надмолекулни структури в разтвор. Водоразтворимите каликсарени с техните относително големи хидрофобни кухини с архитектура наподобяваща формата на ваза са подходящи за формиране на мицели в разтвор с различни съединения "гости".

Цел: Целта на тази работа е изследване влиянието на дължината на алкилиращия радикал върху свойствата на създаденото семейство от сулфонатоалкилирани каликс[4]резорцинарени.

Дискусия:

На основата на неразтворимия във вода С-тетраметилкаликс[4]резорцинарен, синтезиран по оптимизирана методика, е създадено ново семейство от сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарени (схема 1). Използваните сулфоалкилиращи агенти представляват алифатни алдехиди с различна дължина на алкиловата верига (C_2-C_{10}) и смес от натриев метабисулфит и натриев сулфит. Получените сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарени притежават отлична водоразтворимост.

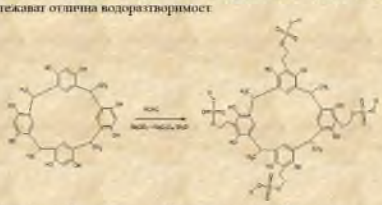
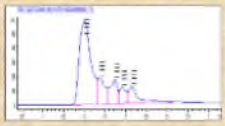


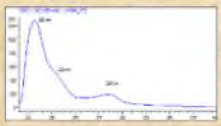
Схема 1. Синтез на сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарени

Синтезираните продукти са охарактеризирани чрез различни инструментални методи и е доказана тяхната структура.

От ВЕТХ хроматограмите на получените продукти (фиг.1) се установи, че се елуират няколко фракции, характеризиращи се с идентични УВ спектри (фиг.2). Вероятно това са различни конформери на сулфонатоалкилираните С-тетраметилкаликс[4]резорцинарени.

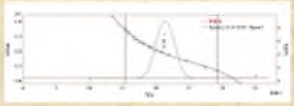


фиг.1. ВЕХТ хроматограма на сулфонатоалкилиран С-тетраметилкаликс[4]резорцинарен



фиг.2. УВ спектър на сулфонатоалкилиран С-тетраметилкаликс[4]резорцинарен

Мономодалните хроматограми (фиг.3) от ГПХ анализите показват получаване предимно на тетрасулфонатоалкилирани продукти с молекулни маси близки до теоретично изчислените (табл.1).



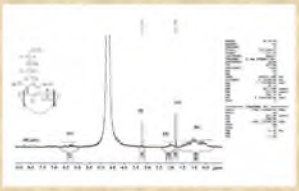
фиг.3. ГПХ хроматограма на сулфонатоалкилиран С-тетраметилкаликс[4]резорцинарен

таблица 1.
Молекулно-масови характеристики на сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарени получени при алкилиране с агент с различна дължина на алкиловата верига

Дължина на алкилиращия агент - R	Теоретична молекулна маса, Da	Молекулно-масови характеристики*		
		Mn (в Da)	Mw (в Da)	D
C_2H_4	877.06	880	1180	1.348
C_3H_6	1000.21	1001	1180	1.141
C_5H_{10}	1143.39	1018	1314	1.2399
C_6H_{12}	1201.48	1070	1235	1.1542
C_7H_{14}	1257.58	1031	1201	1.1443
C_8H_{16}	1313.68	1173	1329	1.1296
C_9H_{18}	1369.80	1260	1366	1.1000
$C_{10}H_{20}$	1425.90	1318	1420	1.0813

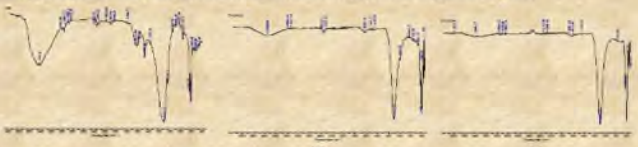
* Молекулно-масовите характеристики са определени чрез ГПХ с двойна детекция (диференциален и УВ рефрактометри (λ=230nm)), колони UltraHydrogel 120Å и 250Å, елуент смес от 16% ацетонитрил и 84% воден разтвор на 0,05% трифлуороцетна киселина, температура 30°C, скорост на елуиране 0,8 ml/min, калибриране с ПЕГ стандарти.

В ^{1}Н ЯМР спектрите на получените продукти се виждат характерните сигнали доказващи структурата на сулфонатоалкилираните каликс[4]резорцинарени. В областта 0,5÷1,6 ppm и 3,1÷3,4 ppm се наблюдават мултиплетни резонансни сигнали отговарящи на протоните от алкилиращия агент (фиг.4).



фиг.4. ^{1}Н ЯМР спектър на сулфонатоалкилиран С-тетраметилкаликс[4]резорцинарен

В ИЧ спектрите с увеличаването на дължината на алкилиращия агент се забелязва постепенно намаляване на интензитета на сигнала при около 3200÷3600 $см^{-1}$, характерен за феноланите ОН групи наличащи се в пръстена и увеличение на интензитета на характерните трептения за сулфо-групите (S=O) при 1150÷1210 $см^{-1}$, както и при 1030÷1060 $см^{-1}$. Поради пространственото пречене адсорбиониите явиши характерни за спрегнатите в пръстена ОН групи намаляват, като характерния максимум при около 3450 $см^{-1}$ се отмества към по-ниски стойности, в резултат на намаляване ефекта на междумолекулните водородни връзки между съседните ОН групи в макроцикъла (фиг.5).

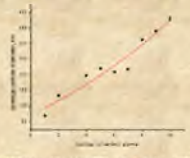


(а) (б) (в)

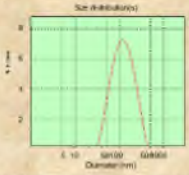
фиг.5. ИЧ спектри на сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарени с различна дължина на алкилиращия радикал: (а) CH_2; (б) C_4H_8 ; (в) C_5H_{10}

Известно е, че С-тетраметилкаликс[4]резорцинаренните образуват в разтвор компактни и стабилни надмолекулни структури под формата на три- или шестмерни капсули, подходящи за използване като контейнери за физиологично-активни вещества. Предполага се, че новосинтезираните сулфонатоалкилирани продукти с различна дължина на алкилиращия радикал ще формират мицели/агрегати с по-рехава надмолекулна структура, поради осъществяващо се пространствено пречене, водещо до понижаване ефекта на водородните връзки между съседните ОН групи в макроцикъла. Това ще засилва взаимодействието между сулфо групите и някои по-отдалечени ОН групи.

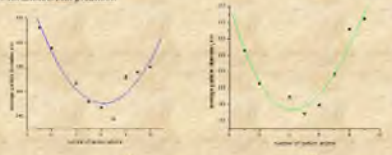
За да се докаже или отхвърли подобна хипотеза са проведени изследвания за определяне размера на частиците, получавани във водните разтвори на сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарени (фиг. 6), както и на натоварените с различна концентрация на моделното физиологично активно вещество (ФАВ) (α-амино-р-хидроксибензил-пеницилин) (фиг. 8.) с динамично разсейване на светлина.



фиг.6. Зависимост на средния размер на надмолекулните каликсаренови агрегати (определени чрез динамично разсейване на светлина, при концентрации 1.10^{-4} mol/l) от дължината на алкиловия радикал.



фиг.7. Графична зависимост на разпределението по размер на частици получени във водни разтвор на сулфонатоалкилирани С-тетраметилкаликс[4]резорцинарен.



(а) (б)

фиг. 8. Зависимост на средния размер на получените каликсарен/α-амино-р-хидроксибензил пеницилин „гостоприемни" структури (схема 2) от моларното съотношение каликсарен/ФАВ: (а) 1÷ 1 и (б) 1÷ 2

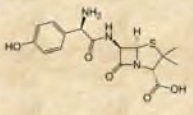


Схема 2. α-амино-р-хидроксибензил пеницилин

Установено е, че формиращите се надмолекулни структури увеличават своя среден размер с нарастване дължината на алкилиращия радикал. Получените агрегати/частици са с направилна форма, според наблюдаваните тенденции към едновременно нарастване на средният им размер (фиг.6) и дисперсност (фиг.7). Включването на α-амино-р-хидроксибензил-пеницилин в гостоприемните сулфонатоалкилирани каликсаренови структури, независимо от концентрацията, води до уплътняване на надмолекулните структури и намаляване на техния среден размер, при дължина на веригата на алкилиращия агент в границите от 3 - 8 въглеродни атома (фиг. 8а). Забелязва се, че при по-големи концентрации на моделното ФАВ тези граници се стесняват (фиг.8.б)

За потвърждаване на тази хипотеза се извършват допълнителни изследвания.

Заключение:

Синтезирани са семейство от сулфонатоалкилирани С-тетраметилкаликс[4]-резорцинарени с различна дължина на алкилиращия агент. Доказана е тяхната структура и е тествана възможността за приложението им като контейнери за модели физиологично-активни вещества.

Благодарности

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CELL ADHESIVE BEHAVIOR OF PVA-BASED HYBRID MATERIALS WITH SILVER NANOPARTICLES AND REMOVAL OF CHROMIUM IONS FROM WATER

R. Bryaskova[1], Z. Todorova[1], N. Lazarova[1], N. Georgieva[1], R. Tzoneva[2]

[1]*University of Chemical Technology and Metallurgy, blvd. Kl. Ohridsky 8, 1756 Sofia, Bulgaria*

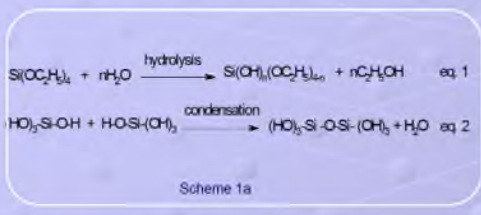
[2]*Institute of Biophysics and Biomedical Engineering,BAS, Acad. G. Bonchev Str., Bl. 21, 1113 Sofia, Bulgaria*

I. INTRODUCTION

Noble metal nanoparticles synthesis attracts significant research interest due to the possible practical application in different areas such as catalysts, biosensors and biotechnologies, microelectronics and optics, biomedicine, nanotechnology. Recently, there has been an increasing interest for the direct synthesis of metal nanoparticles stabilized in a polymer matrix having the potential for their application in biotechnologies and biomedicine. Among different metal nanoparticles, considerable attention is focussed onto silver nanoparticles, because of their unique chemical and physical properties and pronounced antibacterial activity. One possible way for their stabilization is to introduce them into an appropriate polymer matrix, the choice of which is very important for their use in the biomedical field. The use of polyvinyl alcohol (PVA) as a polymer matrix is a popular choice, because of its biocompatibility and excellent chemical and physical properties. However, PVA is very sensitive towards moisture and as a result reduces the film strength that is highly undesirable of the films used for biomedical applications. Significant improvements can be made to the PVA matrix through the incorporation of networked silica using tetraethyl orthosilicate (TEOS) as the precursor via the sol-gel method.

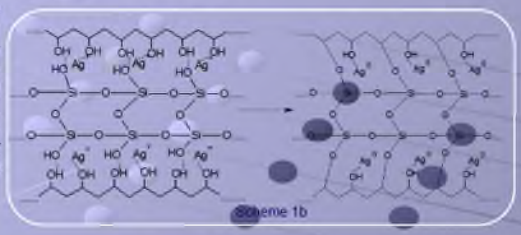
II. STRATEGY:

The synthesis of hybrid materials on the basis of PVA/TEOS matrix with embedded silver nanoparticles was based on *in-situ* formation of silver nanoparticles via thermal annealing of the hybrid films. This was achieved by adding a silver salt ($AgNO_3$), the precursor for silver ions, to the PVA solution leading to coordination of silver ions with hydroxyl groups (-OH) from PVA followed by addition of prehydrolyzed TEOS (in which the substitution of alcoxy groups (OR) with hydroxyl groups (-OH) takes place) (Scheme 1a, eq.1). After the casting of film, polycondensation process proceeds, in which the subsequent Si-O-Si bonds are formed and alcohol or water is realeased depending on the degree of hydrolysis (Scheme 1a, eq.2).



Scheme 1a

The presence of hydroxyl groups in the repeating units of the PVA polymer are expected to produce strong interactions (hydrogen or covalent bonds) with the silanol groups generated from acid catalyzed hydrolysis and polycondensation of TEOS (Scheme 1b). Further, thermal annealing of the films leads to formation of silver nanoparticles as a result of *in-situ* reduction of the Ag+ ions in the PVA/TEOS matrix (Scheme 1b).



Scheme 1b

III. CHARACTERIZATION:

TEM images clearly demonstrate the formation of spherical silver nanoparticles, homogeneously distributed in PVA/TEOS matrix obtained by annealing the films at 100°C for 60 min (Figure 2). The average particle size increased slightly from 5.0 ± 0.7 nm to 6 ± 1.8 nm when the concentration of the $AgNO_3$ in the initial mixture is increased (Figures 1). The histograms illustrate the relatively narrow size distribution and an increase in the average number of the particles per unit area of the films with increasing the silver concentration. Moreover, EDX analysis confirms the formation of the silver nanoparticles by exhibiting a peak at approximately 3 KeV, which is typical for the absorption of metallic silver nanocrystallites due to surface plasmon resonance.

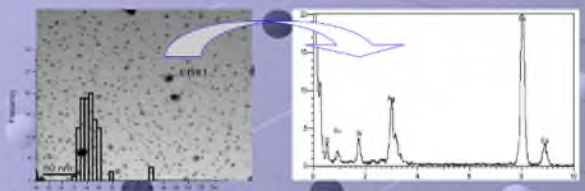


Figure 1. a) TEM image of PVA/AgNps/TEOS films with 0.4% silver concentration heated at 100°C for 60 min., with particle size distribution in the image area; b) EDX spectrum of the PVA/AgNps/TEOS/ with 0.4% silver concentration .

IV. ANTIBACTERIAL ACTIVITY:

The hybrid PVA/AgNps/ TEOS/ materials are further tested for bactericidal activity toward control strains by the Disk Diffusion Method (DDM) in which the inhibition zone is monitored. The microorganisms, involved in the experiment are the etalon strains and they are chosen with the agents from the group of Gram - positive bacteria – *Staphylococcus aureus ATCC 25923*, from the group of Gram – negative enteric bacteria – *Escherichia coli ATCC 25922* and from the group of non-ferment Gram-negative bacteria - *Pseudomonas aeruginosa ATCC 27853*.

Figure 3. Antibacterial activity of PVA/TEOS/AgNps

It is found that all the PVA/AgNps/TEOS films exhibit bactericidal activity by the appearance of an inhibition zone against gram-positive bacteria (*S. aureus*), gram-negative bacteria (*E. coli*) and non-ferment Gram-negative bacteria (*P. Aeruginosa*) (Figure 3).

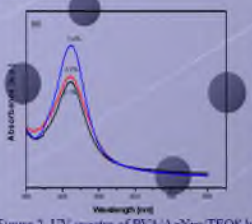


Figure 2. UV spectra of PVA/AgNps/TEOS hybrid materials

The formation of silver nanoparticles is also evidenced from UV-Vis spectroscopy by the appearance of strong absorption bands at 420 nm (Figure 2). The appearance of absorption bands at this wavelength indicates the formation of spherical Ag NPs which is in an accordance with the TEM observations. The absorption of the silver nanoparticles becomes stronger with increasing the silver content from 0.1% up to 0.4%.

V. CYTOTOCITY TEST AND CELL ADHESIVE BEHAVIOUR

The basic material PVA/TEOS exhibited rather high cell viability (85%). The viability of cells cultivated for 24 hours with extracts of hybrid matrices slightly decreased with the increasing of Ag content and became around 70 % for PVA/TEOS/AgNps with 0.9% Ag keeping rather high rate comparing to the positive control (10% viability) (Figure 4). The influence of surface properties of hybrid materials on the adhesive behavior of 3T3 cell line was studied by visualization of actin cytoskeleton of adhered cells. Fig. 5 shows 3T3 cells adhered to polymer materials after 48 hours of incubation. Adhered cells on PVA/TEOS (reference material) after 48 hours incubation formed monolayer areas of well spread cells (Figure 5).

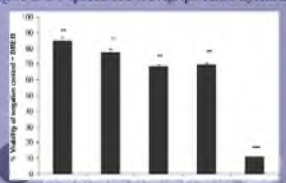


Figure 4. Cytotoxicity of extracts from the materials estimated with MTS test up to 3 days of extraction in DMEM. Positive control (1mM CuCl2 solution).

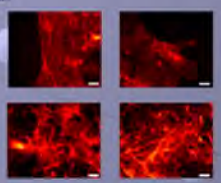


Figure 5. 3T3 cells incubated for 48h on to PVA/TEOS and PVA/TEOS/AgNps films

VI. IMMOBILIZATION OF CELL TRIHOSPORON CUTANEUM ONTO HYBRID MATRICES

The hybrid materials on the basis of PVA, PVA/TEOS and PVA/AgNps/TEOS are used as a metrix for the immobilization of cells *Trihosporon cutaneum R57*. The immobilization is due to their adhesion toward the support as a result of hydrogen bonding between hydroxyl groups (-OH) from PVA and TEOS and hydroxyl and carboxylic groups arising from the cell walls of *Trihosporon cutaneum* (Figure 6).

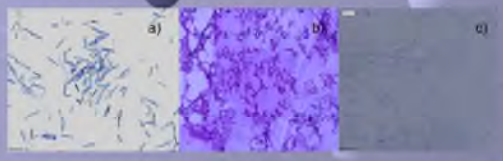


Figure 6. Immobilization of cells: a) free cells; b) cells onto PVA/TEOS matrix; c) cells onto PVA/AgNps/TEOS

During the treatments with 1.0 mM $K_2Cr_2O_7$, the cell culture grew very slowly, showing no typical stage of growth. The high removal efficiency was found in the second hour after metal ions supplementation by PVA-matrices without AgNPs and by PVA-matrices with lowest Ag concentration, where 60 % removal of chromium ions was achieved.

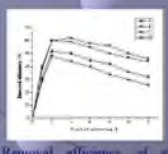


Figure 7. Removal efficiency of strain R57 immobilized onto hybrid materials - on PVA/TEOS (A), on PVA/TEOS 0.2% Ag (B), on PVA/TEOS 0.4%Ag(C), on PVA/TEOS 0.9%Ag(D)

The growth rate of the strain can be evaluated as one of the major factors controlling chromium uptake and accumulation. The biosorption process based on the yeast biomass can be considered as a fast process and the kinetic of chromium ions sorption can be carried out up to 2 hour of the ions supplementation. The results indicated, that the immobilized cells onto hybrid materials PVA/TEOS/AgNps showed tolerance to AgNPs in processes of chromium sorption (Figure 7).

VII. CONCLUSIONS

Novel hybrid material thin films based on polyvinyl alcohol (PVA)/tetraethyl orthosilicate (TEOS) with embedded silver nanoparticles (AgNps) were synthesized using sol-gel method. Silver nanoparticles in PVA/TEOS matrix were prepared by reduction of the silver ions using thermal annealing of the films. TEM images clearly demonstrate the formation of spherical AgNps. The successful incorporation of silver nanoparticles was confirmed using EDX analysis and UV spectroscopy . Further PVA/AgNps/TEOS films were used for immobilization of cells of *Trichosporon cutaneum R57* which are capable to remove metal ions from aqueous solutions. The preliminary results of immobilized cells onto PVA/TEOS matrix showed relatively high sorption capability for ion removal of heavy metals.

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ПОСТЕР № 7

Институт по полимери - Четвърта постерна сесия „ Младите учени в света на полимерите“, 06. 06. 2013 г.

Микромеханични и трибологични изследвания на PP/MWCNTs нанокомпозити

И. Петрова, П. Тодоров, Ю. Цеков, В. Ангелов, И. Борованска, Е. Иванов, Р. Коцилкова

Отворена Лаборатория по Експериментална Механика на микро- и наноструктурни материали (ОЛЕМ) /Институт по механика- БАН

e-mail: ivanka.petrova@yahoo.com ; website: http://www.imbm.bas.bg/index.php/en_US/olem

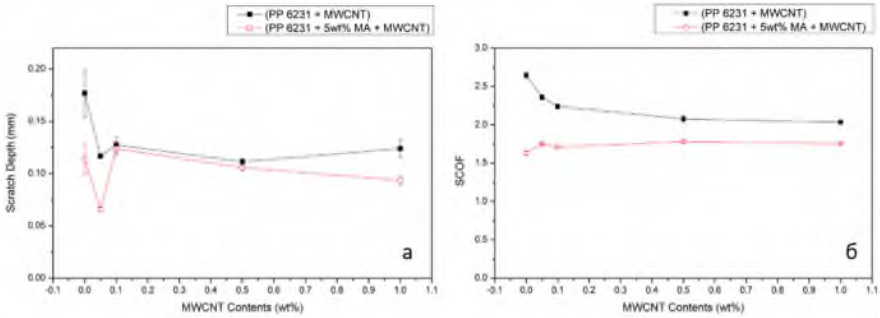
Въведение

Въглеродни нанотръби, се считат за идеална добавка за полимери, поради техните изключителни електрически, термични и механични свойства, които могат да бъдат обяснени с уникалната атомната структура на нанотръбите. Включването на малко количество 0.1 - 1 тегл. % MWCNTs променя значително молекулярната структура на полипропилена. MWCNTs подобряват значително устойчивостта на надраскване, микротвърдостта, модула на Young и коефициента на триене на полипропилена. Това съдейства за промяна на повърхностните свойства посредством увеличаване твърдостта на триене и износване.

Материали и методи

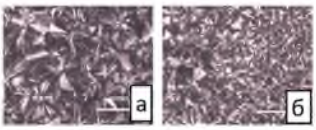
В изследванията са използвани многостенни въглеродни нанотръбички (MWCNTs) като пълнител в матрица от изотактичен полипропилен „Буплен 6231“ (iPP6231) с и без малеинов анхидрид като съвместител на системата. Изследването на микромеханичното и трибологично поведението на PP/MWCNTs нанокомпозити е извършено чрез универсална модулна система UMT (CETR, USA) (Фиг. 1) с различни конфигурации за определяне на силата и коефициента на триене (COF) в голяма част от обема и дълбочината на износване по повърхността.

Фигура 1. Универсален уред за механични и трибологични изследвания.

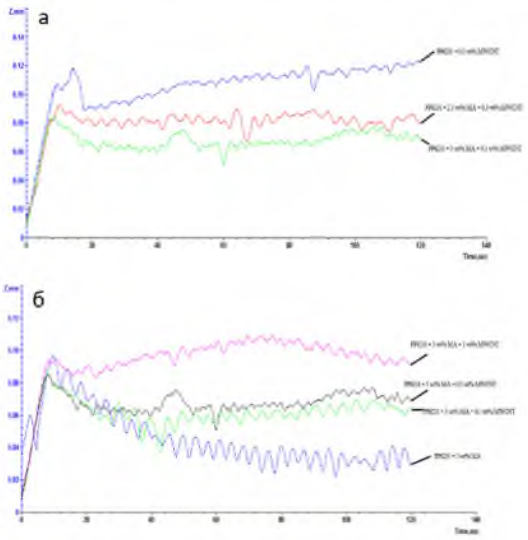


Фигура 2. Зависимост между съдържанието на MWCNT и: а) дълбочина на надраскване б) коефициент на триене при надраскване (SCOF) за iPP6231 с и без малеинов анхидрид.

Фигура 2 показва криви на надраскване, който описват ефекта на MWCNT като пълнител върху iPP матрица. Наблюдава се интересно поведение, при увеличаването на съдържанието на MWCNT в матрицата, без MA води до подобряване на устойчивостта на надраскване (нисък SCOF), поради по-ниското проникване в материала.



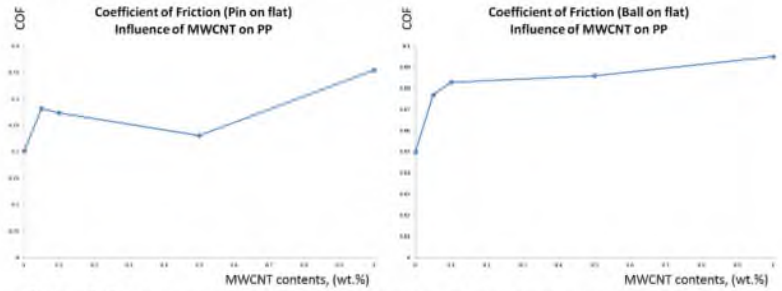
Фигура 3.а) чист iPP6231 и б) iPP6231 + 5 тегл. % MA.



Фигура 4. Поведение при триене чрез надраскване върху плоскост на проби с различно съдържание на MWCNT и на MA.

Междувременно комбинация от iPP с малеинов анхидрид дава по-добри резултати за SCOF, но няма по-нататъшно подобрение, когато се увеличава съдържанието на нанопълнителя. Този ефект може да се обясни с наблюдението, че малеинов анхидрид като цяло втвърдява iPP и променя неговата структура. Оптичните микрографии на фигура 3 показват структурните промени от добавянето на малеинов анхидрид.

Фигура 4 потвърждава, че добавянето на съвместител подобрява поведението на триене при 0,5 тегл. % PP/MWCNT, което може да се обясни с по-добра дисперсия на нанотръбите в iPP. Въпреки това, увеличаването на съдържанието на MWCNT води до леко увеличение на COF, ако се сравни с 5 % MA/PP (фиг.4 б).



Фигура 5. Определяне на коефициент на триене, чрез различни модулни конфигурации

Стойностите на коефициента на триене силно зависят от вида на конфигурацията на модула. На фигура 5 са показани експериментални криви чрез използване на две различни конфигурации - “цилиндър върху плоскост” а) и “топче върху плоскост” б). Въпреки, че двете криви са различни тенденцията за увеличаване на COF с нарастването на съдържанието на MWCNTs се запазва.

Изводи

Добавянето на малко количество MWCNT (под 1 тегл. %) допринася за подобряването на механичните свойства на MWCNT/iPP нанокомпозити. MWCNTs променят значително молекулярната структура на полипропилена като се наблюдава ясна тенденция за подобряване на коефициента на триене с увеличаването на съдържанието на нанотръбичките. Освен това с добавянето на съвместител в системата – малеинов анхидрид се постига по-добра дисперсия на нанотръбичките в матрицата, което допълнително подчертава положителния ефект от добавката.

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ПОСТЕР № 8

Четвърта постерна сесия "Младите учени в света на полимерите" в рамките на проект POLYNNOVA, Институт по полимери – БАН
06 юни. 2013 г.

Структурно охарактеризиране на дву- и трифазни нанокомпозити получени на базата на епоксидна смола.

Верислав Ангелов, Юлий Цеков, Румяна Коцилкова

Отворена лаборатория по експериментална механика на микро- и наноматериали (ОЛЕМ), Направление Физико-химична механика, Институт по механика – БАН
e-mail: verislav@abv.bg

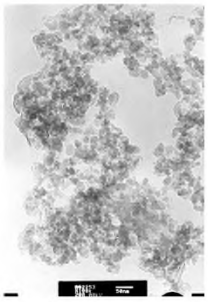
ВЪВЕДЕНИЕ

Трифазните хибридни нанокомпозити, комбиниращи два вида нанопълнители в полимерна матрица, предизвикват широк научен интерес в последните години, поради възможността за получаване на нови материали с мултифункционални свойства. Въпреки това в литературата има малко публикации относно тези материали. Настоящата дисертационна работа има за цел да разработи трифазни нанокомпозити от епоксидна смола с два нанопълнителя от златни наночастици и слоести силикати. Задачата е да се постигнат синергични ефекти при определено съотношение на двата нанопълнителя, водещи до нови физични и механични свойства на трифазните нанокомпозити, които не се наблюдават при двуфазните материали и чистата полимерна матрица.

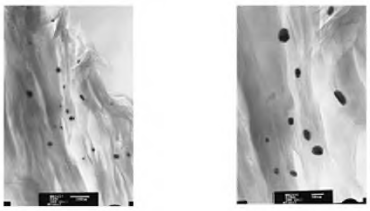
МАТЕРИАЛИ

Материалите използвани в настоящата изследователска работа са органоклей (Cloisite 30B) произведен от от Southern Clay Products, Inc. (USA), тетрахлорзлатна киселина трихидрат (HAuCl4.3H2O) произведена от от Sigma Aldrich, епоксидна смола Epilox T 19-38/500 и съответния втвърдител Epilox H10-30 произведени от LEUNA-Harze GmbH, Germany.

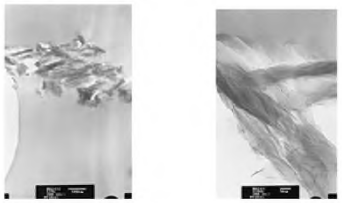
РЕЗУЛТАТИ



Фиг 1. TEM изображение на чист органоклей Cloisite 30B

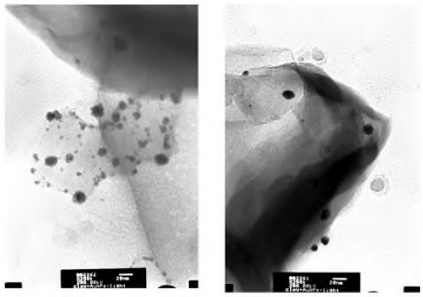


Фиг 4. TEM изображения на трифазен нанокомпозит Epoxy/ Cloisite30B /AuNPs



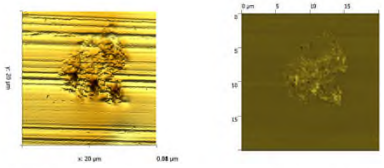
а) увеличение 15 000 пъти b) увеличение 100 000 пъти

Фиг 5 . TEM изображения на двуфазен нанокомпозит Epoxy/ Cloisite30B



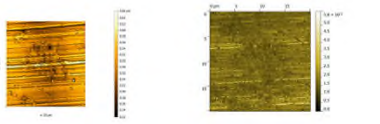
а) AuNPs~ 16nm б) AuNPs~ 11nm

Фиг 2(а,б). TEM изображения на златни наночастици върху субстрат от органоклей (fresh synthesized)



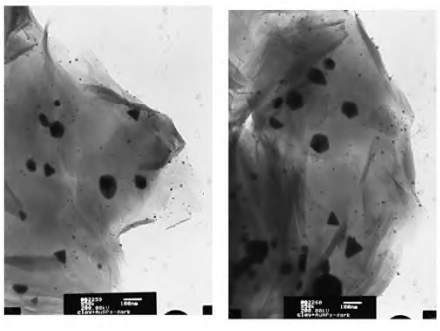
а) 2D Топологично изображение б) 2D Фазово изображение

Фиг 6 (а-б). AFM изображения на трифазен нанокомпозит Epoxy/ Cloisite30B /AuNPs



а) 2D Топологично изображение б) 2D Фазово изображение

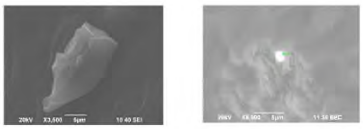
Фиг 7 (а-б). AFM изображения на двуфазен нанокомпозит Epoxy/ Cloisite30B



а) AuNPs~ 73nm б) AuNPs~ 94nm

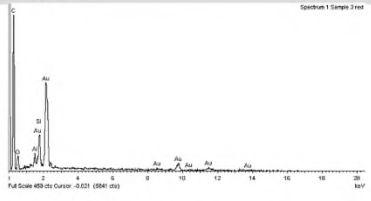
Фиг 3. TEM изображения на декориран органоклей със златни наночастици (след „стареене“)

Получени са златни наночастици с различен размер и форма върху модифицирани слоести силикати (органоклей) от прекурсор тетрахлорзлатна киселина.Установено е, че след „стареене“ в ексикатор под допълнителното действие на температурата и слънчевата светлина се получават по-големи златни наночастици, в сравнение с тези получени веднага след синтеза. Синтезираните златни наночастици върху субстрат от органоклей са изследвани с TEM.
Получени са двуфазен (Epoxy/Cloisite30B) и трифазен (Epoxy/Cloisite30B/AuNPs) нанокомпозити, които са изследвани с TEM, SEM и AFM.

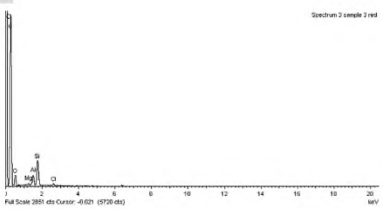


а) Cloisite 30B (SEI режим) б) Златна наночастица (BEC режим)

Фиг 8 (а-б). SEM изображения на трифазен нанокомпозит Epoxy/ Cloisite30B /AuNPs



Фиг 9. EDS спектър на Au



Фиг 10. EDS спектър на Cloisite 30B

ИЗВОДИ

Получен е органоклей (Cloisite30B)/AuNPs декориран със златни наночастици с различен размер и форма. Този нанопълнител е структурно охарактеризиран с TEM. Получени са два нанокомпозита (двуфазен и трифазен) Epoxy/Cloisite30B и Epoxy/Cloisite30B/ AuNPs и също са структурно охарактеризирани чрез TEM, SEM и AFM. Предстои да се изследват техните физични, термични и механични свойства и да се установи връзката структура-свойства, както и да се получат по анологичен начин и други нанокомпозити с по-високо масово съдържание на златни наночастици.

ПОСТЕР № 9

Novel Multifunctional Polyphosphoesters

Anita Bogomilova, Neli Koseva and Kolio Troev

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

Abstract: New functional polyphosphoesters bearing 1,3-dioxolan-2-one and P–H or P–OCH_3 groups, or urethane and hydroxyl groups have been synthesized and characterized. Poly(oxyethylene H-phosphonate) was used as precursor polymer. It was reacted with 4-ethenyl-1,3-dioxolan-2-one through the addition of the polymer P–H groups to the double C-O bond of the cyclic carbonate derivative. The non-reacted P–H groups in the product were further transformed into phosphate P–OCH_3 groups under Atherton–Todd reaction conditions. The 1,3-dioxolan-2-one functions were also modified *via* aminolysis affording new polyphosphoester bearing hydroxyuretane fragments in the side chains. It was found that the addition of the P–H group to the carbon double bond of 4-ethenyl-1,3-dioxolan-2-one proceeded in the presence of peroxides while KF and CdI_2 did not promote the addition reaction.

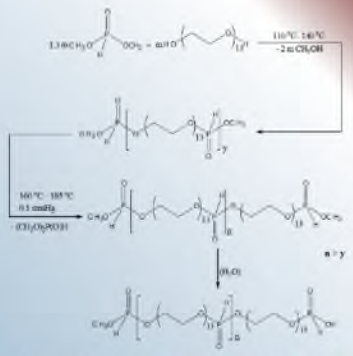
Aim: synthesis and structure elucidation of novel multifunctional polyphosphoesters bearing P–H or P–OCH_3 groups in the main chain and 1,3-dioxolan-2-one rings or hydroxyurethane fragments attached to the polymer backbone through a P–C bond.

1) the precursor poly(oxyethylene H-phosphonate) was modified *via* addition of the polymer P–H groups to the vinyl group of the cyclic carbonate derivative or applying the Atherton - Todd reaction yielding methyl phosphate moieties (P–OCH_3).

2) the aminolysis of the 1,3-dioxolan-2-one rings afforded a polyphosphoester bearing hydroxyurethane fragments in the side chains. Different compounds such as peroxides, KF and CdI_2 were studied as a promoters of the addition reaction of P–H groups to the vinyl group of 4-ethenyl-1,3-dioxolan-2-one. The reaction proceeded with satisfactory yield in the presence of tert-butyl peroxybenzoate

Results and discussion

1) Synthesis and characterization of poly(oxyethylene H-phosphonate),1



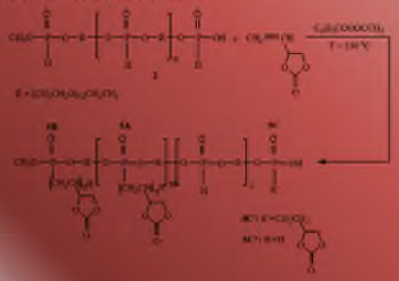
Scheme 1. Reaction pathway used for preparing the poly(oxyethylene H -phosphonate)

Poly(oxyethylene H-phosphonate) **1** was synthesized *via* polytransesterification reaction. **The number average molecular weight (Mn) of the polymer product 1** of Mn = 13 500 g/mol was obtained on the basis of the ^1H and ^{31}P NMR spectral data. GPC measurements confirmed independently the polymer character of **1** displaying good correlation with the NMR data.

2) Synthesis of polyphosphoester bearing five membered cyclic carbonate and P– H groups, 2

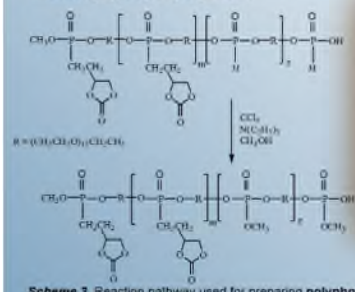
The homolytic addition of the P–H groups of **polymer 1** to the double C=C bond of **4-ethenyl-1,3-dioxolan-2-one** was carried out under the following experimental conditions:

(i) equimolar ratio of the H-phosphonate groups in the polymer to the vinyl carbonate
(ii) tert-butyl peroxybenzoate as initiartor
(iii) a reaction temperature 130 °C



Scheme 2. Reaction pathway used for preparing the polyphosphoester bearing fivemembered cyclic carbonate and P–H groups - polymer 2

3) Synthesis of a polyphosphoester bearing cyclic carbonate and methoxy groups -polymer 3



The P–H groups in the polymer 2 can be feasibly converted into P–OCH_3 groups at room temperature applying the Atherton–Todd reaction. The newly synthesized polyphosphoester 3 possesses two reactive functional groups – the carbonate cycle and the methoxy group. The carbon atom in the latter is an electrophilic centre able to participate in alkylation of amines and in a dealkylation reaction, i.e. reaction with metal salts or hydrogen chlorides. The carbonate cycle can react with amines imparting new functioanality.

Scheme 3. Reaction pathway used for preparing **polyphosphoester bearing cyclic carbonate and methoxy groups – polymer 3**

Two separate runs of the addition reaction were performed !!!

Experiment 1 - the monomer and the initiator were dissolved in toluene and added drop-wise for a period of 4 h. The reaction system was under slow flow of inert gas. The reaction was carried out at 130 °C for a total reaction time of 5 h. In the ^1H NMR spectrum *(Fig. 1)* of the main product, new signals appeared in the region 1.40–3.03 ppm, which can be attributed to the hydrogen atoms in the PCH_2CH_2 segment formed by the addition of the P–H groups in the polymer to the vinyl groups in the cyclic carbonate derivative molecules. Moreover, the signals for the hydrogens from the CH_2=CH– group of 4-ethenyl-1,3-dioxolan-2-one in the region 5.4–5.8 ppm disappeared.

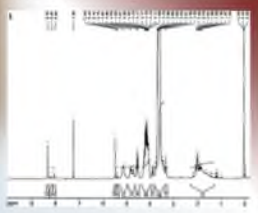


Fig. 1 1H NMR spectrum of polymer 2 (Experiment 1)

Direct evidence for the formation of the new P – C bond in the P–CH_2CH_2 fragment were the two doublets that appear in the $^{13}C\{H\}$ NMR spectrum of 2 *(Fig. 2)* at 20.65 ppm with coupling constant $^1J_{P,C}$= 144.30 Hz assigned to P–CH_2 and at 27.11 ppm with $^2J_{P,C}$= 4.9 Hz attributed to the other carbon atom in the P – CH_2CH_2 group. The signals at 72.39 ppm, 71.04 ppm and 154.60 ppm correspond to the carbon atoms in the 1,3-dioxolan-2-one ring (Fig. 2).

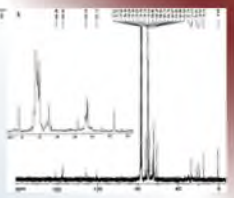
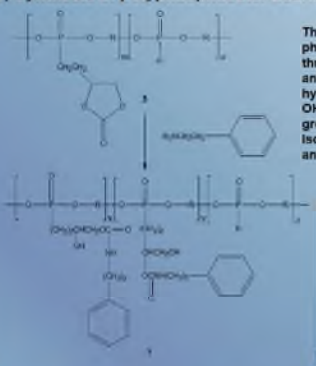


Fig. 2. 13C(H) NMR spectrum of polymer ***2***

4) Synthesis of polyphosphoester bearing hydroxyurethane and P–H groups, polymer 4



The interaction of the polyphosphoester 2 with phenylethylamine at room temperature proceeded through aminolysis of the cyclic carbonate residues and afforded a polyphosphoester 4, bearing hydroxyurethane and P–H groups *(Scheme 4).*The OH and P–H groups of polymer 4 are reactive groups and determine possibilities of 4 to react with isocyanates, esters, anhydrides, aldehydes, ketones and Schiff bases

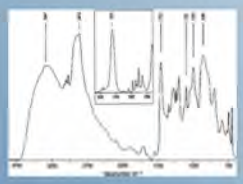


Fig. 4. IR spectrum of 4

Experiment 2 - the addition reaction was carried out in a closed glass reactor and a solvent with higher boiling point was used, i.e. p-xylene. The monomer – initiator solution was added in three portions at intervals of 1 h. Prior the addition of the following portion of the monomer - initiator solution a sample of the reaction mixture was withdrawn for GPC -analysis. The chromatograms of the starting polymer and those of the products at different stages of the reaction are given in Fig. 3

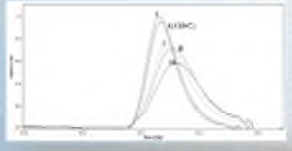


Fig. 3. GPC traces of
- 1 – starting poly(oxyethylene H-phosphonate);
- **1(130 °C)** – poly(oxyethylene H-phosphonate) after melting at 130 °C;
- the reaction mixture of 4-ethenyl-1,3-dioxolan-2-one and polymer **1** under the conditions of Experiment 2:
- I (1 h) – Experiment 2 after 1 h reaction time
- II (2h) – Experiment 2 after 2 h reaction time
- III (3h) – after 3 h reaction time

The change in the reaction conditions favored the isolation of higher molecular weight polymer – Mn = 8 400 g/mol and Mw/Mn = 1.62, in comparison with the product obtained under the conditions of Experiment 1. This result was also evidenced by the spectroscopic data. In the ^{31}P NMR spectrum of the product just a slight increase in the content of chain end groups was observed. A value of Mn = 7800 g/mol was calculated

In conclusion:

It was demonstrated that a common precursor polymer can be transformed into three different polyphosphoesters through feasible modification reactions. Preserving the main structure and composition of the backbone, new functional groups were incorporated into the macromolecules. In addition to the common features the modification imparts new properties to each of the products. The combination of valuable properties listed above renders these new polyphosphoesters as candidates for drug delivery applications.

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Gene delivery systems based on novel comb-like PEI polymers

E. Haladjova[a], S. Rangelov[a], S. Halacheva[c], V. Posheva[b] , V. Maksimova[b]

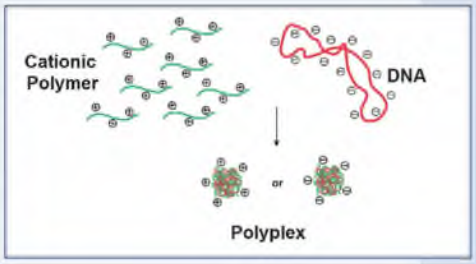
[a] Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
[b] Institute of Molecular Biology Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
[c] Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom
e-mail address: ehaladjova@polymer.bas.bg

Introduction

Gene therapy has gained significant attention over the past two decades as a potential method for treating genetic disorders. Various cationic polymers have been studied as potential DNA carriers. Among them polyethylenimine (PEI) has been found to be a very effective transfection agent; therefore, it is called " the gold standard" for gene transfection. One of the important features of this polymer is the high concentration of positively charged nitrogen atoms that facilitates effective binding and condensation of negatively charged DNA. DNA condensation is a function of the cation-to-anion ratio, e.g. polymer nitrogen-to-DNA phosphate groups or N/P ratio.

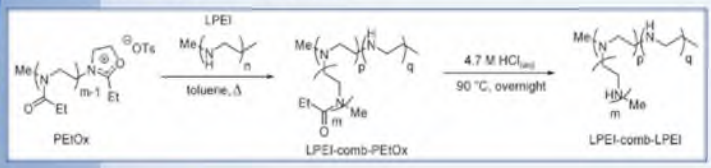
The transfection efficiency and toxicity of PEI based complexes depend on several factors including polymer molecular weight, the structure of the polymer (linear or branched) etc. For example, linear PEI has lower toxicity than branched, but its transfection efficiency is lower. Also, transfection efficiency of PEI polyplexes increases with increasing molecular weight, however high molecular weight polymers result significantly higher cytotoxicity. For these reasons it is important to find and select the appropriate feature polymers which will be able to transfer DNA molecules.

The **aim** of this work is to obtain effective and low toxicity DNA delivery systems based on novel well-defined comblike linear polyethylene imine/linear polyethylene imine (LPEI-comb-LPEI) polymers. Effects of PEI molecular weight and structure on the physical properties of PEI/DNA complexes was also studied.



Polymer synthesis

Comb like LPEI-comb-LPEI polymer have been obtained in two steps: first LPEI was synthesized via ring opening polymerization of 2-ethyl-2-oxazoline followed by acide hydrolysis. After that grafting of PEtOx chains onto a LPEI "initiator core" was accomplished to produce branched LPEI-comb-PEtOx copolymers. These compounds were then hydrolyzed in order to obtain the final LPEI-comb-LPEI polymers.



Polymer	DP of main chain ^{1}H NMR	DP of branches ^{1}H NMR	Degree of grafting ^{1}H NMR	Molecular weight ^{1}H NMR	Zeta mV
$LPEI_{96}$-$comb_5$-$LPEI_{48}$	96	48	5	14 450	15,1
$LPEI_{66}$-$comb_7$-$LPEI_{66}$	66	66	7	22 700	16,5
$LPEI_{20}$-$comb_{20}$-$LPEI_{96}$	20	20	96	83 420	17,5

DNA/Polymer complexation

DNA/polymer complexes (polyplexes) at different N/P ratios were prepared. Appropriate amounts of DNA was added dropwise into the heated at 60° C polymer in aqueous solution under stirring. Two types of DNA were used: Salmon sperm, Mw ~ 2000 bp and plasmid pEGFP-C2, Mw ~ 4700 bp. Hydrodynamic dimentions and effective charge of obtained polyplexes were determined by dynamic light scattering and zeta potential mesurements. The complexes were visualized by transmision electron microscopy.

✓ ssDNA

• $LPEI_{96}$-$comb_5$-$LPEI_{48}$

N/P	Rh, nm	PdI	Zeta mV
1/1	141	0,23	-28,5
2/1	137	0,22	-32,2
4/1	119	0,18	-30,8
6/1	precipitation region		
8/1			
10/1	232	0,24	9,3
12/1	193	0,24	9,0
15/1	120	0,23	7,7
20/1	257	0,23	12,5
25/1	218	0,22	14,3

• $LPEI_{66}$-$comb_7$-$LPEI_{66}$

N/P	Rh, nm	PdI	Zeta mV
1/1	102	0,24	-35,9
2/1	67	0,25	-27,0
4/1	precipitation region		
6/1	330	0,50	3,6
8/1	317	0,50	5,7
10/1	326	0,50	5,5
12/1	180	0,42	6,3
15/1	213	0,44	6,5
20/1	220	0,35	8,1
25/1	241	0,38	6,1

• $LPEI_{20}$-$comb_{20}$-$LPEI_{96}$

N/P	Rh, nm	PdI	Zeta mV
1/1	99	0,24	-22,1
2/1	precipitation region		
4/1			
6/1	234	0,50	12,5
8/1	175	0,24	7,16
10/1	285	0,28	12,9
12/1	180	0,29	17,9
15/1	232	0,23	14,5
20/1	290	0,24	13,7
25/1	298	0,24	12,7

✓ pDNA

• $LPEI_{96}$-$comb_5$-$LPEI_{48}$

N/P	Rh, nm	PdI	Zeta mV
2/1	148	0,23	-27,8
4/1	precipitation		
8/1	244	0,23	4,85
10/1	179	0,22	4,97
12/1	272	0,14	7,11

• $LPEI_{66}$-$comb_7$-$LPEI_{66}$

N/P	Rh, nm	PdI	Zeta mV
2/1	148	0,24	-21,6
8/1	684	0,60	7,25
12/1	162	0,20	4,84

• $LPEI_{20}$-$comb_{20}$-$LPEI_{96}$

N/P	Rh, nm	PdI	Zeta mV
2/1	122	0,23	-33,3
8/1	496	0,48	7,40
12/1	326	0,24	9,47

Discussion

By controlled hydrolysis of PEtOz a series of well defined LPEI-comb-LPEI polymers with different molecular weight and structure was synthezed. Their molecular weight characteristics were determined by ^{1}H NMR and their effective charge were

Polyplexes of different N/P ratios were prepared using these polymers with single stranded or plasmid DNA. We monitored the inherent properties of the resulting complexes such as size and zeta potential as a function of the polymers structure and molecular weight. In a region around stoichiometric conditions (usually N/P around 1) precipitation occurs in the system due to charge neutralization. In our systems this precipitation region is displaced to a higher ratios, due to the fact that at pH 7 only ~ 30% of the nitrogens of PEI are protonated. Depending on the molecular weight characteristics of polymers the precipitation region is about N/P 4÷8. Upon addition of excess of DNA the complexes seem to shrink in size, but exhibit strongly negative charge. Their effective charge change into positive after precipitation region accompanied by an increase in size. Particles with a maximum size and high polydispersity were observed in a region beyond the stoichiometric conditions for $LPEI_{66}$-$comb_7$-$LPEI_{66}$ polymer. This is probably due to its specific structure with more and longer branches than $LPEI_{96}$-$comb_5$-$LPEI_{48}$ thus causing better interaction with DNA molecules even in higher ratios. In the case of $LPEI_{20}$-$comb_{20}$-$LPEI_{96}$ wherein the number and length of branches is the highest we observed a slight decrease in hydrodynamic dimensions and good size distribution in contrast to $LPEI_{66}$-$comb_7$-$LPEI_{66}$. The reason is probably in higher density and length of branches leading to a more inaccessible positive charges for DNA molecules. TEM micrographs show that the resulting DNA/polymer complexes are spherical in shape and their size correspond to this observed by DLS. At the complexes formed with plasmid DNA a similar behavior was observed.

Future goals

✓ Examination of the stability of DNA/polymer complexes
✓ Toxicity determination of polyplexes
✓ Investigations of transfection efficiency of new DNA delivery systems

Acknowledgements
This work was funded by the National Science Fund (Bulgaria) Project DMU 03/30/12.12.2012 and was supported by European Commission project "POLINNOVA"

ПОСТЕР № 11

ДИЗАЙН И ПОТЕНЦИАЛНИ ПРИЛОЖЕНИЯ НА НАНОСТРУКТУРИРАН НЕТЪКАН ТЕКСТИЛ, СЪДЪРЖАЩ ТИТАНОВ ДИОКСИД

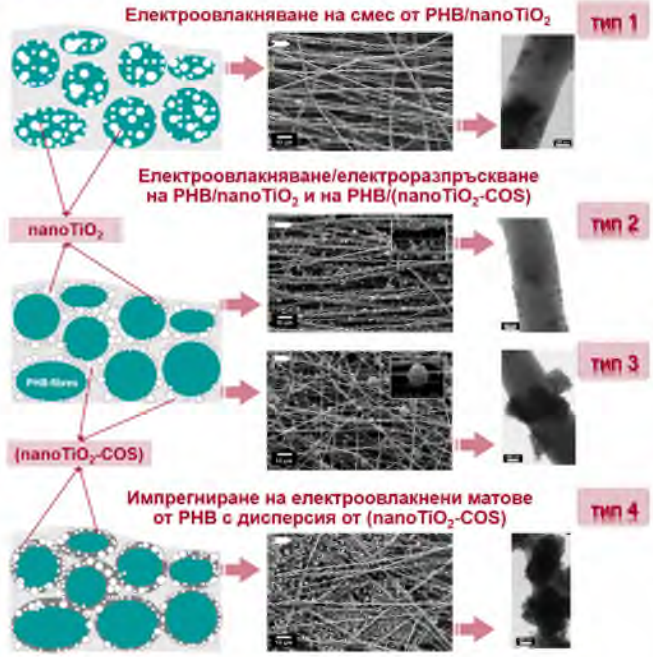
Е. Корина, О. Стоилова, Н. Манолова, Ил. Рашков

Лаборатория Биологично активни полимери, Институт по полимери – БАН

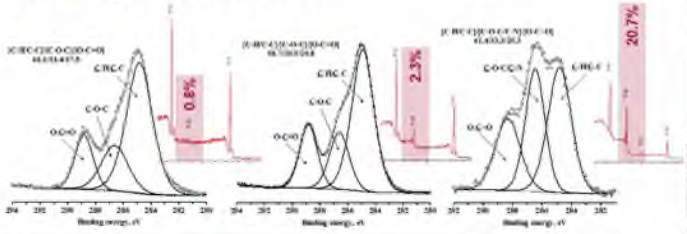
Целта на работата е да се създадат нови мултифункционални хибридни материали от биоразградими полимери и неорганични наночастици (TiO_2). Подходът се състои в комбиниране на методите електроовлакняване, електроразпръскване и импрегниране, което осигурява насочено моделиране на дизайна на получените материали. По този начин ще се създаде набор от хибридни биоматериали с желани фотокаталитични и антибактериални свойства, и с възможност за приложение като подложки за развитие на клетки в тъканното инженерство.

Наноструктуриран нетъкан текстил

За получаване на различните типове наноструктуриран нетъкан текстил са използвани биосъвместимите и биоразградими поли(3-хидроксибутират) (PHB), наноразмерен титанов диоксид (nanoTiO_2) и олигомери на природния полизахарид хитозан (COS).



Химичният състав на повърхността на хибридните материали е оценен чрез рентгенова фотоелектронна спектроскопия. В общия XPS спектър и на четирите типа материали се наблюдават фотоемисионни ивици за C1s (285 eV), O1s (532.5 eV) и Ti2p (458.5 eV).

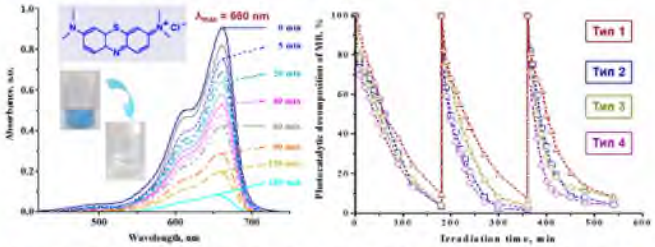


Изводи

- комбинирането на методите електроовлакняване, електроразпръскване и импрегниране е лесен и ефективен подход за получаване на хибридни влакнести биоматериали от PHB, nanoTiO_2 и COS с насочено моделиран дизайн;
- получените нови типове хибридни биоматериали комбинират фотокаталитичните свойства на nanoTiO_2 и проявяват значителен биоциден ефект спрямо бактерии (*E. coli*);
- различните типове хибридни материали са биологично съвместими с човешки мезенхимни стволови клетки и осигуряват благоприятна среда за тяхното развитие.

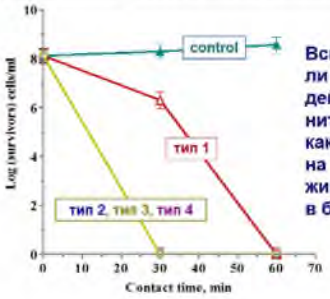
Фотокаталитична активност

За проследяване на фотокаталитичната активност на различните типове влакнести материали е използвано багрилото метиленово синьо като моделен органичен замърсител.



И четирите типа хибридни биоматериали показват отлична стабилност и запазват почти напълно фотоактивността си и след трикратно използване; в края на третия цикъл се постига около 95% разграждане на багрилото с материалите от тип 3 и 4, а с тези от тип 1 и 2 – около 92%.

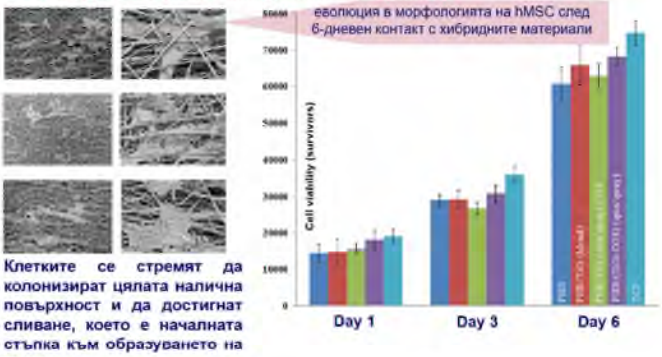
Антибактериална активност



Всички типове хибридни материали показват силно бактерицидно действие спрямо Грам отрицателните бактерии *Escherichia coli*, както показва оценяването на броя на микроорганизмите, останали живи след инкубиране на матовете в бактериалната суспензия.

Съвместимост с hMSC

Проследено е влиянието на nanoTiO_2, както и на топографията на различните типове хибридни биоматериали върху развитието на *човешки мезенхимни стволови клетки (hMSC)*.



Клетките се стремят да колонизират цялата налична повърхност и да достигнат сливане, което е началната стъпка към образуването на тъкан.

Литература

E. Korina, O. Stoilova, N. Manolova, I. Rashkov, *Macromol. Biosci.*, DOI: 10.1002/mabi.201200410 (2013)

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Европейски съюз

POLY(OXYETHYLENE AMINOPHOSPHONATE)S: SYNTHESIS, NMR CHARACTERIZATION AND BIOLOGICAL EVALUATION

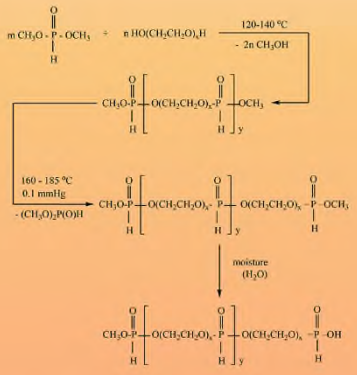
Ivanka Kraicheva, Elitsa Vodenicharova, Anita Bogomilova, Ivelina Tsacheva, Kolio Troev
Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
evodenicharova@polymer.bas.bg

INTRODUCTION

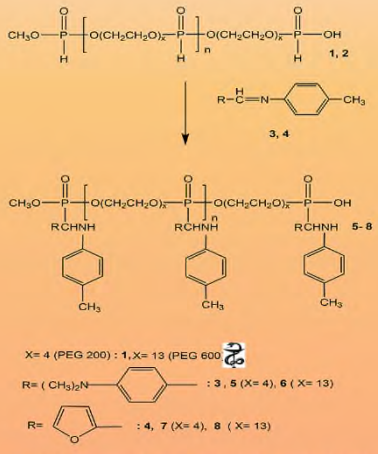
The development of new effective polymeric systems for the treatment of different diseases, including cancer, diabetes, ischemia, severe combined immunodeficiency, neurodegenerative, offers enormous possibilities to the advanced pharmaceutical technology. The polymer-drug conjugates have much potential to improve the therapy of variety human pathologies, solving major problems in medicine, such as the toxic effects of the drugs and the duration of drug action.
Among the numerous macromolecular systems studied for drug delivery purposes, the polymers with phosphorus ester (C-O-P-O-C) repeating units in the backbone occupy a particularly important place, because they can degrade into biocompatible and non-toxic components under physiological conditions. These polymers possess reactive functional groups in their backbone, which allows for conjugation of bioactive molecules to the chains and gives much opportunities for the preparation of new drug delivery systems with improved therapeutic indexes. On the basis of poly(oxyethylene H-phosphonate)s we synthesized poly(oxyethylene aminophosphonete)s – alternating copolymers built only of aminophosphonate units with potential biological activity and non-toxic poly(ethylene glycol) links. Poly(oxyethylene aminophosphonate)s were synthesized via addition of poly(oxyethylene H-phosphonate)s to the Schiff bases N-(4-dimethylaminobenzylidene)-p-toluidine and N-furfurylidene-p-toluidine. The polymer analogous reaction proceeded in the presence of catalytic amount of CdI_2, as well as without a catalyst. The cytotoxicity of the synthesized poly(aminophosphonate)s was tested against a panel of human tumor cell lines, using cisplatin as reference cytotoxic agent.

The immobilization of aminophosphonates to biodegradable polymer carriers like poly(oxyethylene H-phosphonate)s appears a promising approach in the design of new polymer drug carriers, as well of new polymers with own activity.

CHEMISTRY



Scheme 1. Synthesis of polymer carrier



Scheme 2. Synthesis of poly(oxyethylene aminophosphonate)s 5-8

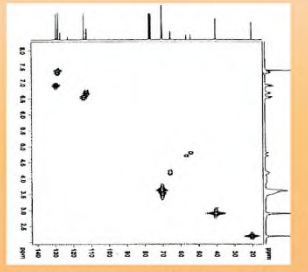
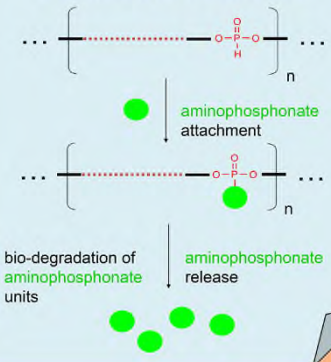


Figure 1. CH COSY diagram of poly(oxyethylene aminophosphonate) 5 in $CDCl_3$

POSSIBLE APPLICATION



PHARMACOLOGY

The compounds were tested for cytotoxicity in a panel of human tumor cell lines, representative for some clinically important types of neoplastic diseases, namely HL-60 (acute promyelocyte leukemia), its multi-drug resistant sub-line HL-60/DOX (characterized by overexpression of MRP-1 efflux pump), LAMA-84 and K-562 (chronic myeloid leukemias). The cells were exposed to serial dilutions of the tested compounds for 72 h and thereafter their viability was assessed using the MTT-dye reduction assay. The clinically used antineoplastic drug cisplatin was used as reference cytotoxic agent.

Table 1. Cytotoxic effects of the poly(oxyethylene aminophosphonate)s 5-8 vs. the clinically applied antineoplastic drug cisplatin, as assessed by the MTT-dye reduction assay after 72 h continuous exposure.

Compounds	IC_{50} (μmol/L)			
	HL-60	HL-60/Dox	LAMA-84	K-562
5	105. 9	> 400. 0	> 400. 0	> 400. 0
6	19. 2	27. 2	17. 2	14. 9
7	19. 9	20. 4	14. 0	15. 2
8	14. 2	14. 4	12. 3	13. 7
Cisplatin	7. 8	14. 5	18. 2	25. 7

CONCLUSION

Novel poly(oxyethylene aminophosphonate)s 5-8 were synthesized via addition of poly(oxyethylene H-phosphonate)s 1 and 2 to the Schiff bases N-(4-dimethylaminobenzylidene)-p-toluidine 3 and N-furfurylidene-p-toluidine 4.

The polymers 5-8 were obtained on the basis of biodegradable polymer carriers 1 and 2 consist only of aminophosphonate (active substance) and non-toxic poly(ethylene glycol) units.

The polymers 5-8 have coordination centres in their repeating units and can be used as new biodegradable polymer carriers for physical immobilization of bioactive substances.

Compounds 6-8 caused prominent cytotoxic effects with low micromolar IC_{50} values, whereas 5 was only marginally cytotoxic.

In spite of the Schiff base fragment however, in all sub series of compounds the reduction of the length of the PEO miety from 13 to 4 units was consistent with significant reducitpon in relative potency and in case of 5 with dramatic loss of activity.

The established cytotoxicity of compounds 6-8 is similar or comparable to that of the reference drug cisplatin findings give us reason to consider the presented compounds as a novel class of aminophosphonate-based cytotoxic agents.

Acknowledgement: This investigation has been financially supported by POLINNOVA Project funded under the FP7 Grant Agreement No 316086

POLYMER GENE DELIVERY VECTORS ENCAPSULATED IN THERMALLY SENSITIVE BIOREDUCIBLE SHELL

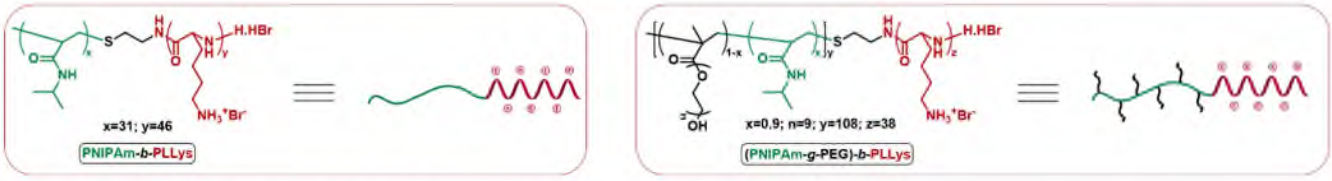
Emilya D. Ivanova[1,2], Nadya I. Ivanova[3], Margarita D. Apostolova[3], Sevdalina C. Turmanova[2], Ivaylo V. Dimitrov[1]

[1]Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
[2]Burgas Prof. Assen Zlatarov University, Y. Yakimov St. 1, Burgas 8010, Bulgaria
[3]Institute of Molecular Biology, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

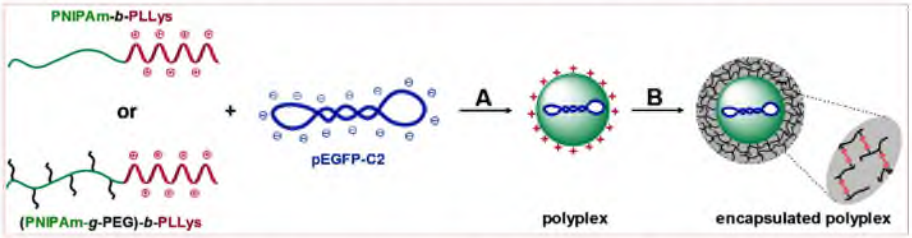
POLYMER-BASED NON-VIRAL GENE DELIVERY SYSTEMS HAVE GAINED SIGNIFICANT ATTENTION DURING THE LAST TWO DECADES DUE TO THEIR GREAT POTENTIAL FOR THE DEVELOPMENT OF SAFE AND EFFICIENT VECTORS. MOST OFTEN CATIONIC POLYMERS ARE USED TO FORM POLYELECTROLYTE COMPLEX (POLYPLEX) WITH THE NEGATIVELY CHARGED DNA MOLECULE IN ORDER TO CONDENSE AND PROTECT THE GENETIC MATERIAL DURING ITS TRANSPORT THROUGH THE BLOOD STREAM TO THE TARGET CELLS. THUS, NUMEROUS COPOLYMERS OF VARIOUS ARCHITECTURES WITH CATIONIC SEGMENTS AND POTENTIAL BIOMEDICAL APPLICATION WERE SYNTHESIZED. THE RATIONAL DESIGN OF POLYMER VECTORS MUST PROVIDE AN OPTIMAL BALANCE BETWEEN TWO CONFLICTING ATTRIBUTES, NAMELY, PROTECTION AND RELEASE OF NUCLEIC ACIDS. CONSEQUENTLY, THE NEXT LEVEL IN CONSTRUCTING EFFICIENT GENE DELIVERY SYSTEMS BASED ON POLYPLEXES INVOLVES VARIOUS METHODS FOR THEIR FURTHER STABILIZATION. VERY RECENTLY WE INTRODUCED A NEW METHOD FOR POLYPLEX STABILIZATION THROUGH AN AQUEOUS SEEDED RADICAL POLYMERIZATION OF ACRYLIC MONOMER, PERFORMED ON THE POLYPLEX SURFACE IN THE PRESENCE OF DIFFERENT CROSS-LINKERS.

HEREIN WE PRESENT THE POLYPLEX FORMATION BETWEEN PLASMID DNA AND HYBRID COPOLYMERS OF DIFFERENT ARCHITECTURES FOLLOWED BY THEIR ENCAPSULATION IN BIOREDUCIBLE POLYMER SHELL. THE SYSTEMS in-vitro TRANSFECTION ABILITIES HAVE BEEN EVALUATED.

I Hybrid block and graft copolymers synthesized *via* controlled polymerization methods



II Polyplex formation and its encapsulation in bioreducible outer polymer layer

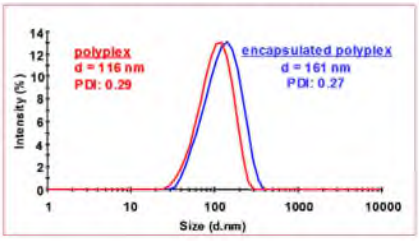


A – Polyplex formation at room temperature in aqueous media (charged groups molar ratio [N]/[P] = 20).

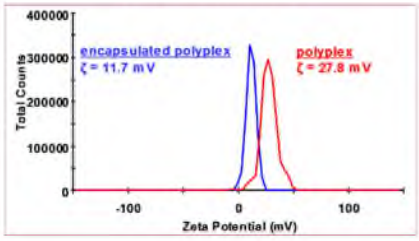
B – Polyplex encapsulation through seeded radical copolymerization of *N*-isopropylacrylamide and PEG-diacrylate in the presence of bioreducible cross-linker *N,N'*-bis(acryloyl)cystamine (BAC) at 70°C in water .

III Characterization of polyplex formed between (PNIPAm-*g*-PEG)-*b*-PLLys and pDNA before and after the encapsulation step

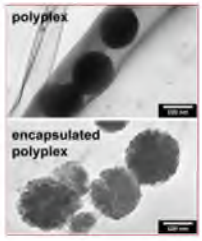
❑ *Size distribution by intensity*



❑ *Zeta potential distribution*

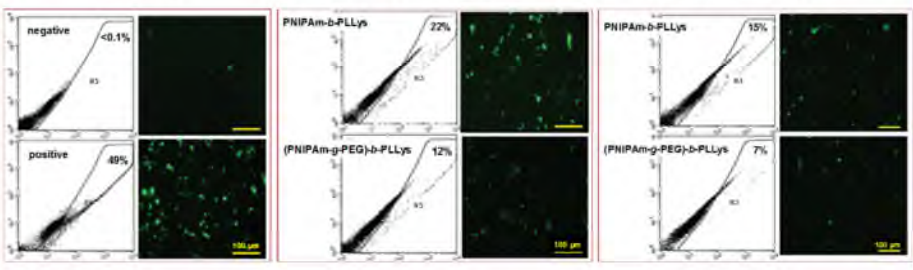


❑ *TEM images*



IV *In-vitro* transfection evaluation

❑ *Controls* ❑ *Polyplexes* ❑ *Encapsulated polyplexes*



CONCLUSIONS

- Nanosized polyplexes between rationally designed hybrid copolymers and pDNA were successfully formed, characterized and their transfection abilities were evaluated.
- The polyplexes were further stabilized through the formation of an additional bioreducible cross-linked polymer shell.
- The encapsulated polyplexes showed reduced transfection efficiency as compared to the corresponding polyplexes. However, the results are encouraging in the search of the optimal balance between DNA protection during the transport and its release into the cells. Finding the best compromise between these conflicting requirements is essential for the construction of an efficient gene delivery system.

The financial support from the Bulgarian National Science Fund (project *DO 02-247/2008*) is gratefully acknowledged.

ПОСТЕР № 14

NANOSTRUCTURED POLYMER ELECTROLYTE MEMBRANES FOR FUEL CELLS

Filip Ublekov[1], Hristo Penchev[1], Maya Staneva[1], Vassil Georgiev[1], Ivan Radev[2], Vesselin Sinigersky[1]

[1]Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria,
[2]Zentrum für BrennstoffzellenTechnik ZBT GmbH Carl-Benz-Str. 201, D-47057 Duisburg, Germany

correspondence authors: ublekov.philip@gmail.com

Introduction

Poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (PBI) is an amorphous polymer with high thermal stability. It was initially developed by Celanese Co. as a fire-resistant fiber. In 1995 it was founded that after treatment with strong acids (sulfuric, phosphoric etc.) PBI becomes proton conductive and can be regarded as a solid polymer electrolyte. Since then great efforts have been made involved in preparation of phosphoric acid doped PBI for PEM fuel cells in order to improve proton conductivity and mechanical properties. Phosphoric acid (PA) has a high boiling point, high thermal stability, and high proton conductivity even in its anhydrous form (Scheme 1). PA content is one of the three main factors that affects the properties of PA doped PBI membrane. The proton conductivity of the membrane increases with increasing PA content. The major factors determining the properties of such membranes are temperature and humidity.

Materials and Methods

Poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (PBI) was supplied by BASF Fuel Cell GmbH as 15 wt. % solution in N,N-dimethylacetamide (DMAc) (inherent viscosity-1.26 $dL.g^{-1}$). Organomodified montmorillonite (MMT, Cloisite®30B) clay was used as filler. It was dispersed in the PBI/dimethylacetamide solution by ultrasonic treatment for up to 1h at 60°C (Scheme 2). From this solution, containg nanosized MMT, films were cast using doctor blade. After drying, the obtained self-supporting membranes were doped with PA at room temperature (about 3 mol PA per PBI unit). In this way PBI/PA membranes, containing 0.1, 0.3 and 0.5 and 1.0 wt% nanostructured MMT, were prepared.

Results and Discussion

A successful approach of incorporating organo-modified montmorilonite (MMT) into PBI matrix have been used. The good dispersability of MMT after ultrasonic treatment in DMAc gave us the opportunity to obtain nanocomposite films of PBI/MMT with concentration of incorporated MMT 0.1, 0.3, 0.5 and 1 wt.%. The diffractograms of the samples shows no diffraction peaks of MMT, which confirms exfoliated nanocomposite structure (Fig.1). The membranes of PBI/MMT showed increased degree of swelling after PA doping up to 420% at RT. The mechanical properties of the obtained composite membranes were measured and compared with that of the pristine PBI membrane. The results from this measurements show complex improvement of the mechanical properties of the novel nanocomposite membranes. The membranes studied were adjusted in four electrode cell placed in the conditioning chamber of the *EasyTest Cell*. The result from conductivity measurements of composite membrane PBI/MMT, doped with PA to degree of swelling 420 mas.%, show conductivity of 126 $mS.cm^{-1}$ at 160°C and 20% relative humidity (Table 1).

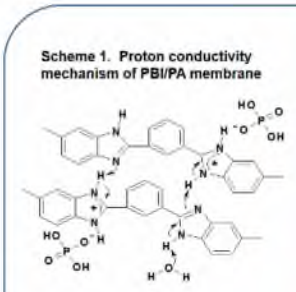
Summary

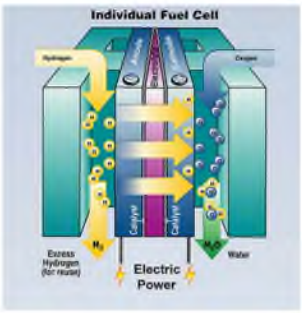
Several novel nanocomposite PBI membranes with incorporated MMT as inorganic laminar filler were prepared and characterized. Due to the low concentrations of the incorporated MMT as laminar nano-fillers, the innovation-pending method gives vast opportunities for preparation of nanocomposite PBI membranes with improved properties, suitable as high temperature PEM for fuel cell applications.

Acknowledgement

Acknowledgement: The authors would like to thank the Bulgarian Science Fund (Project PemHydroGen, ДТК 02/68) for funding the research and EU project POLINNOVA, № 316086 for funding the presentation of the results.

Scheme 1. Proton conductivity mechanism of PBI/PA membrane





The proton conductivity increases with increasing temperature and humidification. However, PBI/PA membranes suffer from inferior mechanical properties at high PA content and high temperature. Thus, it is difficult to maintain the mechanical strength of PBI composite membranes with high PA content at high temperature, which influences the proton conductivity of the membrane. Many efforts have been focused on further improvement of the mechanical properties of PBI membranes. For the operation of PEM-FCs at temperatures above 160°C solid polymer electrolytes with improved mechanical properties are needed. The objective of this study was to prepare nanocomposite membranes, based on polybenzimidazole, doped with phosphoric acid (PBI/PA membranes).

Scheme 2. Preparation of PBI/MMT phosphoric acid doped nannocomposites

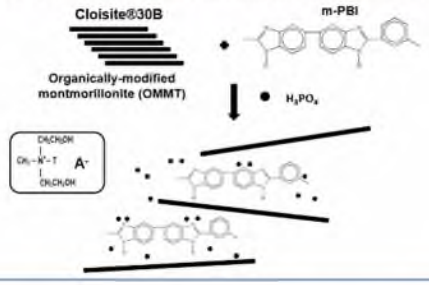


Table 1. Nanocomposites PBI/MMT membranes - mechanical and electrical properties

Membrane samples	Young's modulus, [Mpa]	Elongation at break, [%]	Degree of swelling, 85% H_3PO_4	Proton conductivity, $mS.cm^{-1}$			
				RH 5%	RH 10%	RH 15%	RH 20%
pure PBI	104	37	320 %	-	-	-	83
PBI/MMT 0.1 wt.%	133	60	370 %	53	71	83	107
PBI/MMT 0.3 wt.%	131	69	390 %	51	60	72	84
PBI/MMT 0.5 wt.%	117	86	420 %	68	86	103	126
PBI/MMT 1 wt.%	129	70	370 %	70	95	104	114

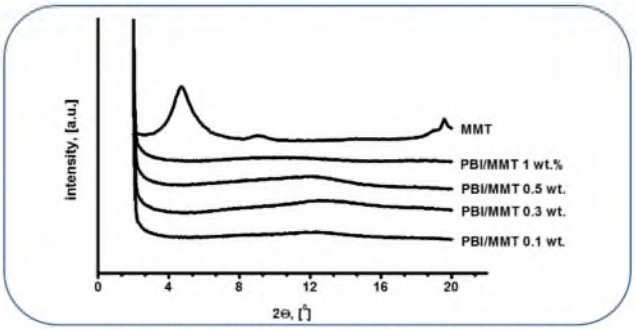


Figure 1. WAXS patterns of PBI/MMT nanocomposites with different weight ratio

ПОСТЕР № 15

Лекарство-доставящи системи на основата на поли(акрилова киселина)-поли(ε-капролактон)-поли(акрилова киселина) триблокови съполимери

Георги Л. Георгиев[a], Петър Петров[a], Симона Димчевска[b], Катерина Горачинова[b]

[a]Лаборатория „Структура и свойства на полимерите", Институт по полимери - БАН, ул. "Акад. Г. Бончев", бл.103А, 1113 София, България.

[b]Факултет по фармация, Университет "Св. Св. Кирил и Методий", ул. Воднянска 17, 1000 Скопие, Македония.

Email: ggeorgiev@polymer.bas.bg

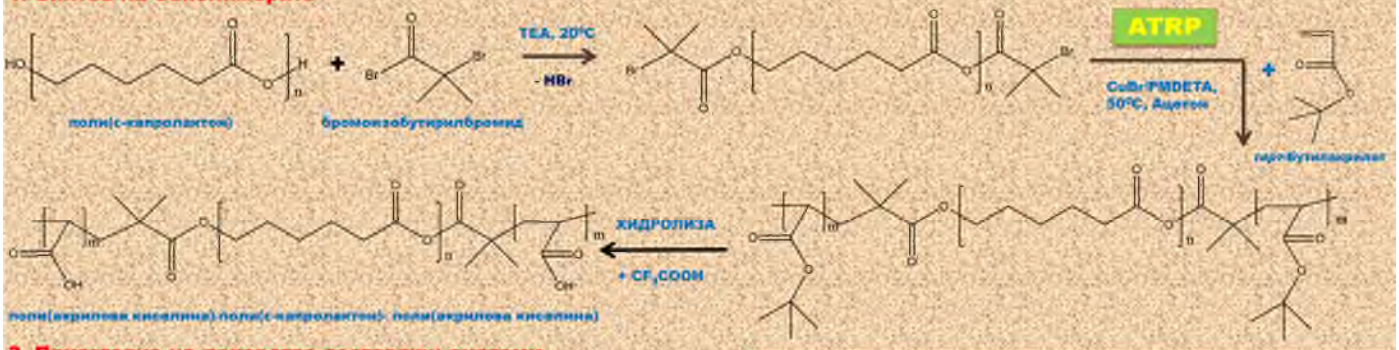
ВЪВЕДЕНИЕ:

Химиотерапията представлява лечение на злокачествени тумори с медикаменти потискащи механизмите на деление и размножаване на туморните клетки. За съжаление лечението води до множество странични ефекти, тъй като прилаганите медикаменти са клетъчни отрови и за здравите клетки на организма. С цел минимизиране на страничните ефекти и подобряване на фармакокинетиката се разработват различни наноразмерни частици(мицели, везикюли, липозоми и др.) като носители на противотуморни лекарства.

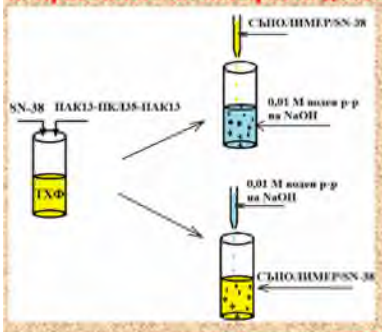
Целта на настоящата работа е да се изследват поли(акрилова киселина)-поли(ε-капролактон)-поли(акрилова киселина) триблокови съполимери като носители на лекарства за противотуморно лечение. Наличието на хидрофобен блок от кристализиращ поли(ε-капролактон) придава на мицелите кинетична стабилност при физиологична температура и при многократно разреждане, т.е. мицелите не дисоциират спонтанно. Също така поли(ε-капролактон)-а е биоразградим, което улеснява отделянето на съполимера от организма след определено време. От друга страна хидрофилните блокове от поли(акрилова киселина) придават стабилност на системата чрез електростатични сили на отблъскване.

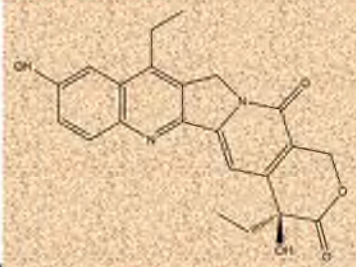
СТРАТЕГИЯ:

1. Синтез на съполимерите



2. Приготвяне на лекарство-доставящи системи





Лекарствена субстанция SN-38

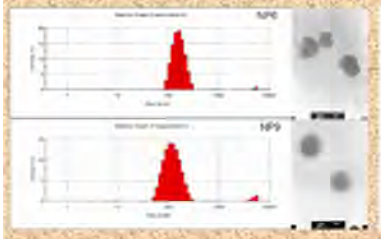
РЕЗУЛТАТИ:

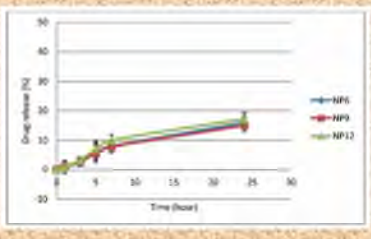
Зададен състав	Получен състав	$Mn^{1H\,NMR}$ (g/mol)	Mn^{GPC} (g/mol)	Mw/Mn
$Пт\text{-}БА_{18}\text{-}ПКЛ_{36}\text{-}Пт\text{-}БА_{18}$	$Пт\text{-}БА_{13}\text{-}ПКЛ_{36}\text{-}Пт\text{-}БА_{13}$	7 300	19 200	1,13
$Пт\text{-}БА_{18}\text{-}ПКЛ_{70}\text{-}Пт\text{-}БА_{18}$	$Пт\text{-}БА_{11}\text{-}ПКЛ_{70}\text{-}Пт\text{-}БА_{11}$	10 800	24 600	1,17
$ПАК_{19}\text{-}ПКЛ_{36}\text{-}ПАК_{19}$	$ПАК_{13}\text{-}ПКЛ_{36}\text{-}ПАК_{13}$	5 900	-	-
$ПАК_{18}\text{-}ПКЛ_{70}\text{-}ПАК_{18}$	$ПАК_{11}\text{-}ПКЛ_{70}\text{-}ПАК_{11}$	9 600	-	-

*елуент ТХФ, универсални Пт-БА стандарти

Код на пробата	pH	SN-38 (mg)	$ПАК_{13}\text{-}ПКЛ_{36}\text{-}ПАК_{13}$(mg)	EE*	Съдържание на SN-38
NP1	10,5	1	12,5	(%) ± SD	(%) ± SD
NP2		2	12,5	31 ± 0,52	3,1 ± 0,1
NP3		3	12,5	37 ± 0,9	6,4 ± 0,4
NP4		5	12,5	8 ± 0,3	2,19 ± 0,12
NP5	10	1	12,5	17,5 ± 0,4	7,28 ± 0,3
NP6		2	12,5	79,35 ± 1,3	7,8 ± 0,25
NP7		3	12,5	45,6 ± 0,6	7,17 ± 0,2
NP8		5	12,5	55,5 ± 0,81	14,4 ± 0,32
NP9	9,5	1	12,5	34,3 ± 0,7	15,5 ± 0,3
NP10		2	12,5	71,36 ± 1	8,32 ± 0,2
NP11		3	12,5	44,88 ± 0,53	7,82 ± 0,31
NP12		5	12,5	44,24 ± 0,47	12,21 ± 0,23
NP13	10	5	12,5	46,25 ± 0,48	18,37 ± 0,21

*ефективност на енкапсулиране определена чрез високоефективна течна хроматография.





ИЗВОДИ:

Приготвянето на съполимери чрез контролирана полимеризация с пренос на атом позволи получаване на добре дефинирани симетрични триблокови съполимери. Определени са оптималните условия за получаване на лекарство-доставящи системи, като са варирани pH на средата и изходното съотношение съполимер/SN-38, ефективността на енкапсулиране и съдържанието на SN-38 в мицелите. Изследвани са размерите и *In vitro* освобождаването на лекарство-доставящите системи с най-добра стабилност - NP6 и NP9. Резултатите показват, че те са подходящи за приложение в химиотерапията.

Благодарности: Изследователската работа бе финансирана от Фонд "Научни изследвания" (проекти **ДНТС/Македония 01/2** и **Б 01/25.2012**) и от Европейската комисия (проект **POLINNOVA**)

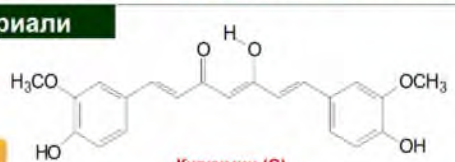
ПОСТЕР № 16

Микровлакнести материали от полимлечна киселина и куркумин, получени чрез електроовлакняване

Гюлджан Якуб, Антония Тончева, Невена Манолова, Илия Рашков
Лаборатория Биологично активни полимери, Институт по полимери - БАН

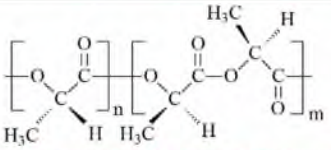
Цел Изследване на възможността за включване на куркумин (С) в микровлакнести материали от поли(L-млечна-съ-D,L-млечна киселина) (PLA) и от PLA/полиетиленгликол (PEG) чрез електроовлакняване.

Използвани материали



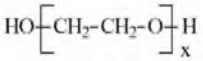
Куркумин (С)

Природен продукт с антибактериално, противосъсирващо, антиоксидантно и противотуморно действие



поли(L-млечна-съ-D,L-млечна киселина) (PLA)

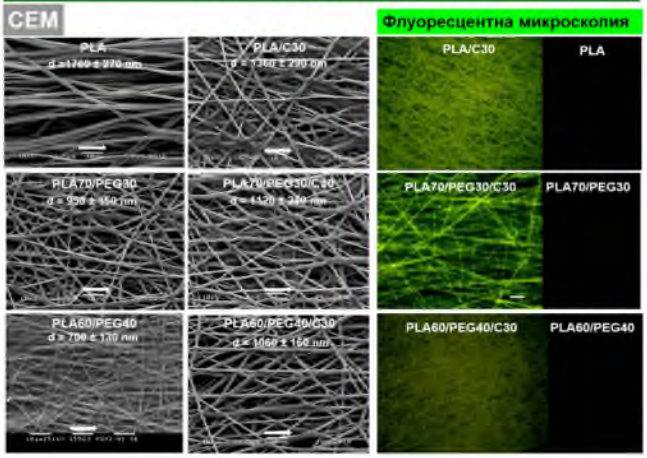
Биологично поносим и биологично разградим полимер от възобновяеми източници

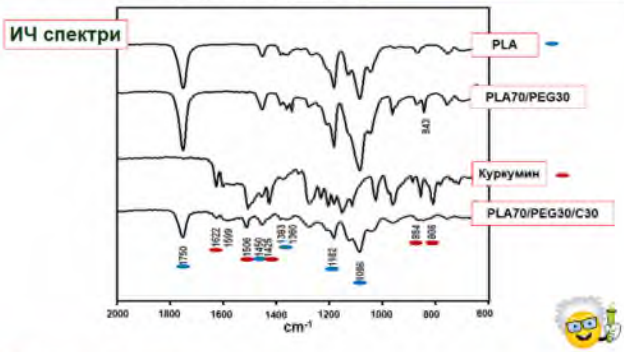


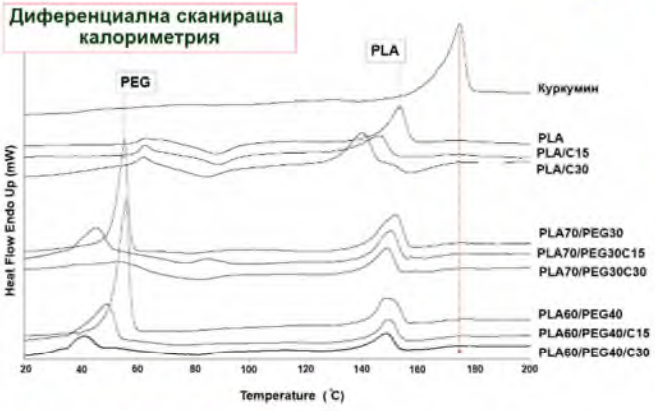
полиетиленгликол (PEG) MW 2000 g/mol

Нетоксичен, биосъвместим полиетер

Охарактеризиране





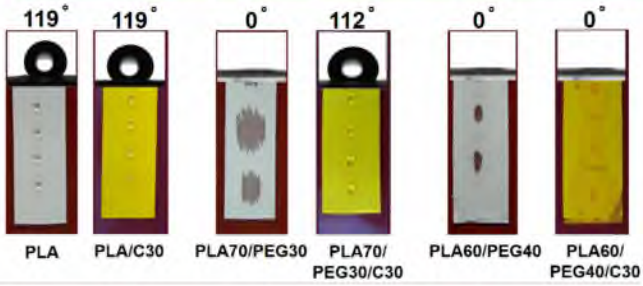


Антикоагулантно действие на куркумин

Широка тромбоеластограма: процес на съсирване на кръвта

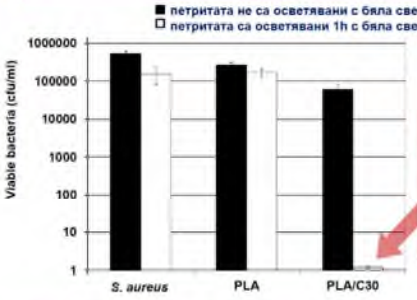
Свиване на тромбоеластограмата: куркумин проявява антикоагулантно действие спрямо човешка кръв

Ъгли на омокряне на матовете



за сравнение са посочени ъглите на омокряне на филми със същия състав

Антибактериална активност



Куркуминът проявява антибактериално действие спрямо патогенния микроорганизъм *S. aureus* при облъчване на мат от PLA/C (С - 30 мас.%) с бяла светлина

Заключение

Получени са микровлакнести материали от PLA и от PLA/PEG, съдържащи куркумин. Резултатите от диференциална сканираща калориметрия показаха, че във влакната куркуминът се намира в аморфно състояние. Доказано е също така и антикоагулантното действие на куркумин, отделящ се от матовете. Влакната от PLA, съдържащи куркумин проявяват антибактериална активност (*S. aureus*), а влакната от PLA/PEG/куркумин, проявяват слаба антибактериална активност.

Благодарност

Г.Я. благодари на договор "Полинова" за финансовата помощ.

За контакти: rashkov@polymer.bas.bg

ПОСТЕР № 17

АНТИБАКТЕРИАЛНИ МАТЕРИАЛИ ОТ ЕЛЕКТРООВЛАКНЕН ПОЛИКАПРОЛАКТОН, МОДИФИЦИРАН С ПОЛИЕЛЕКТРОЛИТЕН КОМПЛЕКС ПОЛИАКРИЛОВА КИСЕЛИНА - *N,N,N*-ТРИМЕТИЛХИТОЗАН ЙОДИД

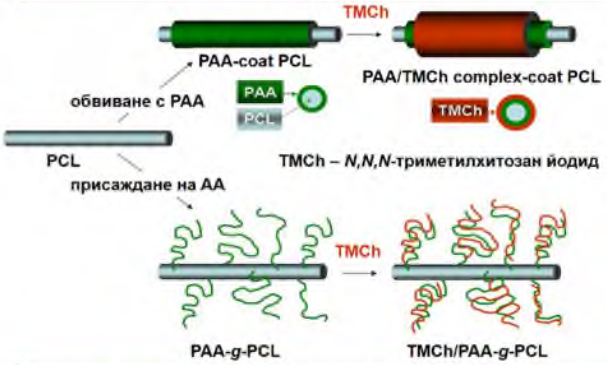
К. Калинов[1], М. Игнатова[1], В. Максимова[2], И. Рашков[1], Н. Манолова[1]

[1]Лаборатория Биологично активни полимери, Институт по полимери, БАН, 1113 София

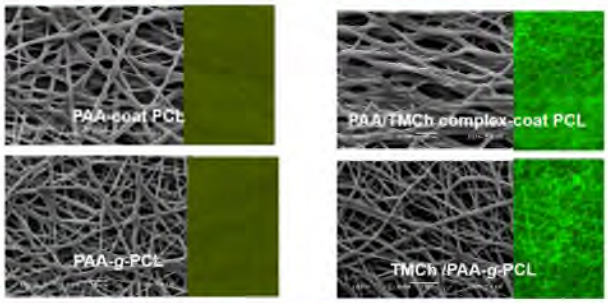
[2]Институт по молекулярна биология, БАН, 1113 София

Известно е, че кватернизираните производни на хитозана имат висока антибактериална активност. Тези поликатиони образуват полиелектролитни комплекси с поликиселини. Съчетаването на ценните свойства на електроовлакнените микровлакнести материали на PCL с тези на *N,N,N*-триметилхитозан йодид и на полиелектролитния му комплекс с полиакриловата киселина е подходящо за създаването на нов тип материали за лечение на рани, антимикробни филтри и др.

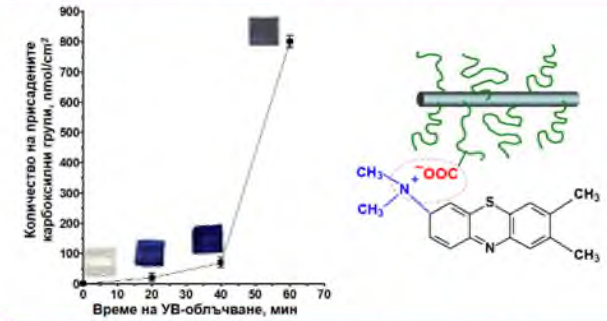
Подходи при получаването на влакнести материали с антибактериални свойства



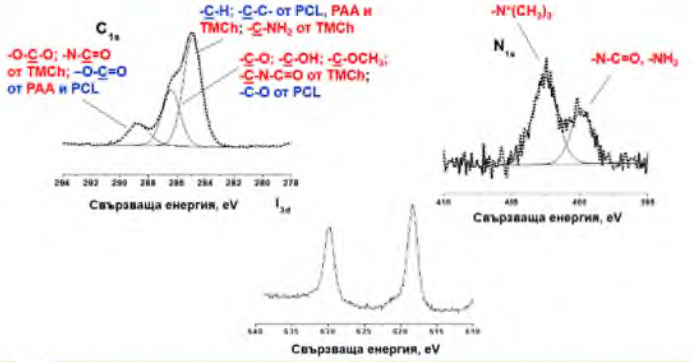
СЕМ и флуоресцентни микрографии на модифицираните матове от PCL



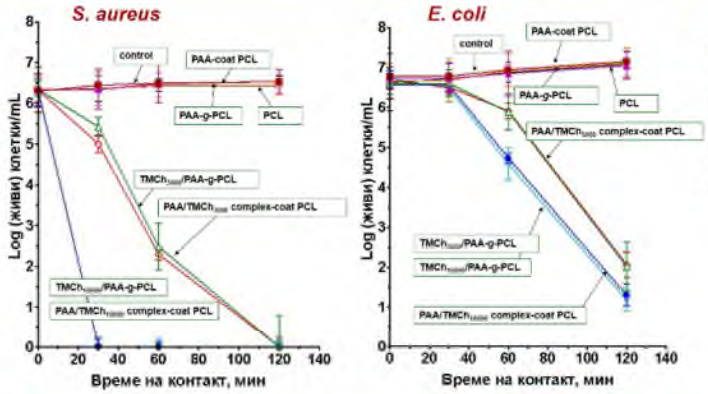
Влияние на времето на УВ-облъчването при присадителната полимеризация на AA върху влакната



Рентгенови фотоелектронни спектри на модифицираните матове



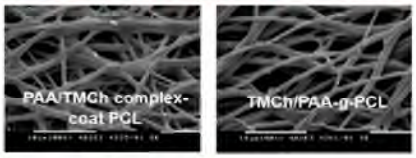
Оценяване на антибактериалната активност на матовете



Отнасяния на матовете спрямо патогенни бактерии

Пролиферация на *S. aureus* върху немодифицираните матове

Потискане на адхезията на *S. aureus* върху модифицираните матове



Изследванията са разработени с финансовата подкрепа на Фонд Научни изследвания (Договор ДВЦП 02/2 - UNION) към МОМН. К. К. изказва благодарност на ОП-РЧР, Договор BG051PO001-3.3.06 - 0006 към Европейския социален фонд, както и на проект Polinnova за отпечатването на постера.

За контакти: kkalinovlbap@gmail.com; rashkov@polymer.bas.bg; manolova@polymer.bas.bg; mil_ign@yahoo.com

ИЗВОДИ: Модифицирането на повърхността на матовете от PCL с тънък филм от полиелектролитен комплекс (ПЕК) PAA/TMCh, както и присаждането на PAA върху матове от PCL с последващото образуване на комплекс между TMCh и присадената PAA, е обещаваща стратегия за получаване на антибактериални влакнести материали. Покритите с ПЕК влакнести материали от PCL потискат в значителна степен развитието на Грам-положителни бактерии (*S. aureus*) и Грам-отрицателни бактерии (*E. coli*). Покритието от ПЕК води и до потискане на адхезията на патогенни бактерии. Тези нови материали са подходящи за редица приложения в биомедицинската практика напр. активни покрития за рани, антимикробни филтри и други.

ПОСТЕР № 18

Получаване и охарактеризиране на микровлакна от полиакрилонитрил с включени наночастици от ZnO чрез електроовлакняване

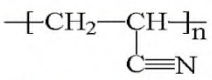
Мария Кънчева, Антония Тончева, Илия Рашков, Невена Манолова
Лаборатория Биологично активни полимери, Институт по полимери - БАН

Цел **Получаване на микровлакна от полиакрилонитрил (ПАН) с включени наночастици от ZnO (10 мас.% и 30 мас.%) чрез електроовлакняване. Изследване на влиянието на количеството на включените във влакната наночастици от ZnO, както и вида им (повърхностно обработени или не) върху морфологията на влакнестия материал от ПАН**

Апаратура за електроовлакняване

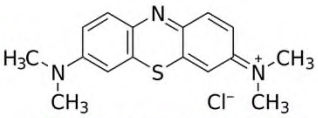
Материали

ZnO → Zano® 20+3 естерофункционален
ZnO → Zano® 20 необработен
ZnO → Zano® 20+2 аминофункционален



Полиакрилонитрил (ПАН)

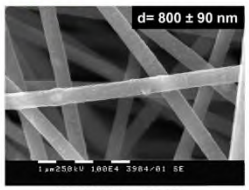
ZnO е съвместим с околната среда неорганичен пълнител, притежаващ антибактериани свойства. Използва се за обработка чрез фотокатализа на текстилни отпадъчни води, съдържащи рекативни багрила.



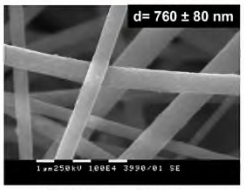
Метиленово синьо (МС)

Охарактеризиране

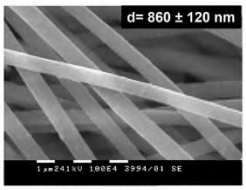
СЕМ



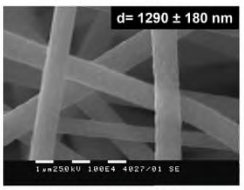
ПАН/Zano® 20 (10 мас.%)



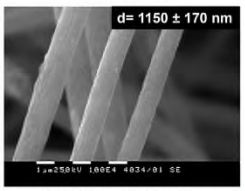
ПАН/Zano® 20+2 (10 мас.%)



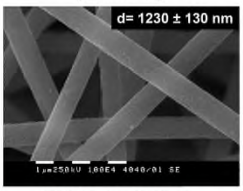
ПАН/Zano® 20+3 (10 мас.%)



ПАН/Zano® 20 (30 мас.%)

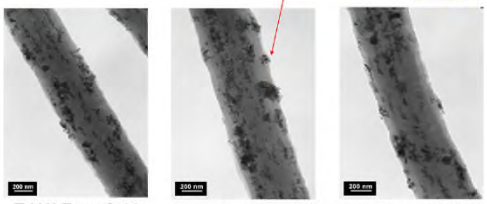


ПАН/Zano® 20+2 (30 мас.%)

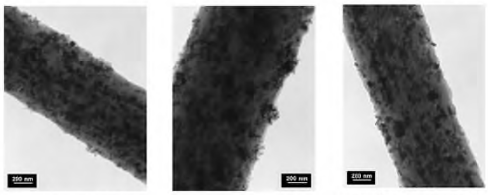


ПАН/Zano® 20+3 (30 мас.%)

TEM



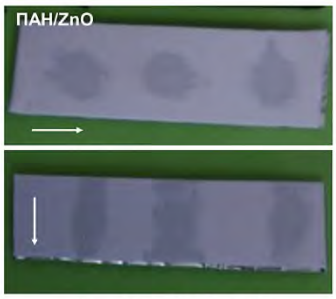
ПАН/ Zano® 20 (10 мас.%) | ПАН/ Zano® 20+2 (10 мас.%) | ПАН/Zano® 20+3 (10 мас.%)



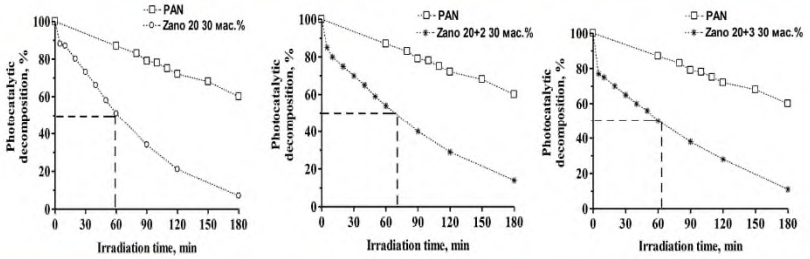
ПАН/Zano® 20 (30 мас.%) | ПАН/Zano® 20+2 (30 мас.%) | ПАН/Zano® 20+3 (30 мас.%)

С повишаване на концентрацията на включените във влакната наночастици средният диаметър на влакната се увеличава.

Фотокаталитично разграждане



Контактен ъгъл = 0°



Заключение

Получени са цилиндрични бездефектни микровлакна от ПАН с включени наночастици от ZnO (10 мас.% и 30 мас.%). TEM и EDX анализите показаха равномерно разпределение на частиците ZnO в обема и по повърхността на влакната. От проведените опити за определяне на контактния ъгъл на омокряне спрямо вода беше установено, че всички проби са хидрофилни. Влакнестите материали, съдържащи Zano®20 проявяват най-добра фотокаталитична активност и разлагат 50% от багрилото за около 1 час. На тези, с включени Zano®20+2 и Zano®20+3, е необходимо повече време, за да разградят 50% от багрилото МС.

Европейски съюз

М. К. благодари на проект ПОЛИНОВА за средствата за разпечатване на постера

За контакти: rashkov@polymer.bas.bg

ПОСТЕР № 19

Forth poster session «Young Researchers in the World of Polymers», June 6th, Institute of Polymers-BAS, Sofia

POLYMER ELECTROLYTE MEMBRANES FOR FUEL CELLS – PBI containing immobilized sulphonic acid groups

Maya Staneva[a], Christo Penchev[a], Filip Ublekov[a], Vesselin Sinigersky[a], Elefteria Lefterova[b]

[a] *Institute of Polymers – Bulgarian Academy of Sciences (IP-BAS), Acad. G. Bonchev Street, bl. 103A, 1113 Sofia, Bulgaria;*

[b] *Institute of Electrochemistry and Energy Systems – Bulgarian Academy of Sciences, Acad. G. Bonchev Street, bl. 10, 1113 Sofia, Bulgaria*

Corresponding author: mstaneva@gmail.com

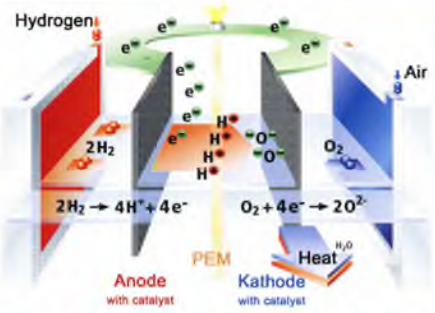
Introduction

The polymer electrolyte membrane fuel cell (PEM FC) generates electricity from an electrochemical reaction in which oxygen (air) and a fuel (e.g. hydrogen) combine to form water and heat (Scheme 1). The polymer electrolyte membrane (PEM) is the heart of the fuel cell. PEM FC with membrane, containing sulfonic acid groups (-SO_3H) are usually operated at temperatures up to 80 °C and high relative humidity (up to 100%).

The proton conductivity is determined by the concentration of the –SO_3H groups, the water contents in the membrane and the working temperature.

The most widely used sulfonated membrane - Nafion® is very expensive (700 USD/m^2. During the last decades considerable effort from industry and academia have been involved in the development of new membranes, containing -SO_3H groups. Different sulfonated polymers (polyether ether sulfones and ketons, polybenzimidazole etc) have been synthesysed and their properties as solid polymer electrolytes studied.

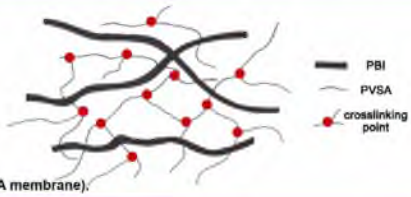
Here we present a new approach for the immobilization of –SO_3H groups in a polymer matrix – preparation of semi interpenetrating networks – polybenzimidazole (PBI), containing cross-linked polyvinylsulfonic (PBI/CrPVSA membranes).



Scheme 1. Polymer electrolyte membrane fuel cell (PEMFC)

Objectives

- ✓ To develope a procedure for cross-linking vinylsulfonic acid in a PBI matrix.
- ✓ Preparation of membranes, comprising a semi-interpenetrating network of PBI and cross-linked polyvinylsulfonic acid (PBI/CrPVSA membranes, Scheme 2).
- ✓ Characterization of the membranes:
  - ✓ chemical structure;
  - ✓ proton conductivity.

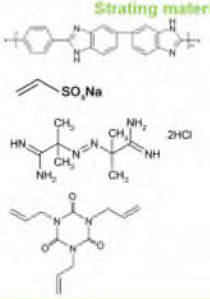


Scheme 2. PBI, containing cross-linked PVSA (PBI/CrPVSA membrane).

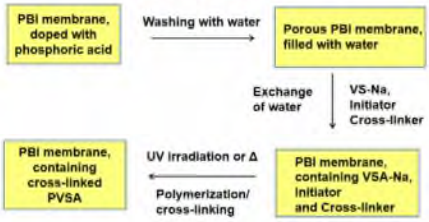
Results

Preparation of membranes

Strating materials:



Preparation procedure



The procedure developed involves the following steps:

1. Preparation of PBI membrane, doped with phosphoric acid (PA): PBI/PA membrane (5 wt.% p-PBI, 95 wt.% 70% PA).
2. Washing the PBI/PA membrane with water – porous PBI membrane, filled with water.
3. Exchange of water: the membrane from step 2 is immersed in a bath, containing water, 25 or 50 wt.% VSA- Na salt (VS-Na), initiator and cross-linker. The result is a PBI membrane, containing the desired reagents.
4. Polymerization/cross-linking of VS-Na in the PBI matrix:
   - ✓ thermally initiated – thermal treatment at 90 °C for a defined time (up to 4 days)!;
   - ✓ initiated by UV light - UV irradiation of the membrane for a defined time (1h).
5. Washing the treated membrane with water – removing unreacted reagents.
6. Treatment in 5%HCl – conversion of the –SO_3Na in –SO_3H.

Characterization of the PBI/CrPVSA membranes

Crosslinking method	mol –SO_3H groups per mol PBI (crosslinked membrane)
Thermal crosslinking – 2 days	1,6
Thermal crosslinking – 4 day	6,9
UV crosslinking – 25 % VS-Na	1,2
UV crosslinking – 50 % VS-Na	2,5

1. Chemical composition:

Contents of cross-linked PVSA (water insoluble) – gravimetrical determination: a piece of the starting PBI/PA membrane was washed with water, dried and solid contents determined. The PBI/CrPVSA membrane was treated in the same way and the weight of water insoluble PBI+CrPVSA determined. From the weight uptake according to the weight of the starting PBI film the weight ratio cross-linked PVSA/PBI was determined and therefrom the number –SO_3H groups per mol PBI (crosslinked membrane) was calculated.

2. Proton conductivity measurements:

The proton conductivity measurements were performed in special cell for membrane test, under wet gas flow. Conductivity of the membranes was determined by impedance spectroscopy - Impedance analyzer Newtons4th PSM1730 FRA § Impedance Analysis Interface was used. Measurements were performed in frequency range -1MHz-1Hz with 10 points per decade.

As expected, the proton conductivity depends on the contents of –SO_3H groups in the membranes. The membrane, containing 6.9 mol –SO_3H groups per PBI repeat unit exhibited the highest conductivity - 32 mS.cm^{-1}.

Conclusion

- ✓ Using an original procedure, membranes from pPBI, containing cross-linked PVSA have been prepared;
- ✓ Two methods (Thermal and UV irradiation) have been used for the initiation of polymerization/cross-linking of VPA-Na salt in the PBI matrix;
- ✓ High concentrations of immobilized (water insoluble) –SO_3H groups have been achieved – up to 6.9 groups per PBI repeating unit;
- ✓ The membranes prepared are of good quality and thermally stable;
- ✓ Proton conductivity increases with increasing the contents of –SO_3H groups in the mebrane;
- ✓ The highest proton conductivity was measured for the membrane with 6.9 VSA groups per PBI repeating unit - 32 mS.cm^{-1}.

Acknowledgement

The authors would like to thank the Bulgarian Science Fund (Project PemHydroGen, ДТК 02/68) for funding the research and EU project POLINNOVA, № 316086 for funding the presentation of the results at Forth poster session «Young researchers in the World of Polymers», June 6th, Institute of Polymers, Sofia, Bulgaria.

NOVEL MICROFIBROUS MATERIALS BASED ON POLYLACTIDE AND POLY(BUTYLENE SUCCINATE) PREPARED BY ELECTROSPINNING

Nikoleta Stoyanova[a], Rosica Mincheva,[b] Dilyana Paneva,[a] Nevena Manolova,[a] Philippe Dubois [b], Iliya Rashkov [a]

[a] Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria
[b] Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons – UMONS, Place du Parc 20, B-7000 Mons, Belgium

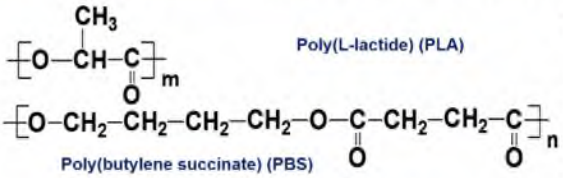
Materials of biodegradable and non-toxic biocompatible aliphatic polyesters such as polylactide and poly(butylene succinate) (PBS) attract increasing interest. Recently, using electrospinning, which is an effective tool for one-pot preparation of fibrous materials under mild and non-destructive conditions, we have prepared new materials from a stereocomplex formed between a high molar mass poly(L-lactide) and copolymers of poly (D-lactide) and PBS [1].

AIM

Preparation of new fibrous materials from poly(L-lactide) (PLA) and poly(butylene succinate) (PBS) homopolymers, their characterization and evaluation of their properties in order to estimate the possibilities for their application.

USED MATERIALS

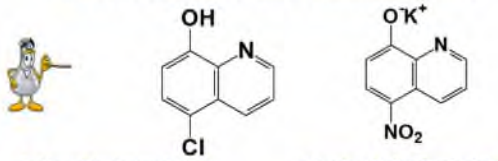
Biodegradable, biocompatible and non-toxic polymers



Poly(L-lactide) (PLA)

Poly(butylene succinate) (PBS)

Model drugs: broad-spectrum antibacterial agents



5-chloro-8-hydroxyquinoline (5Cl8HQ)

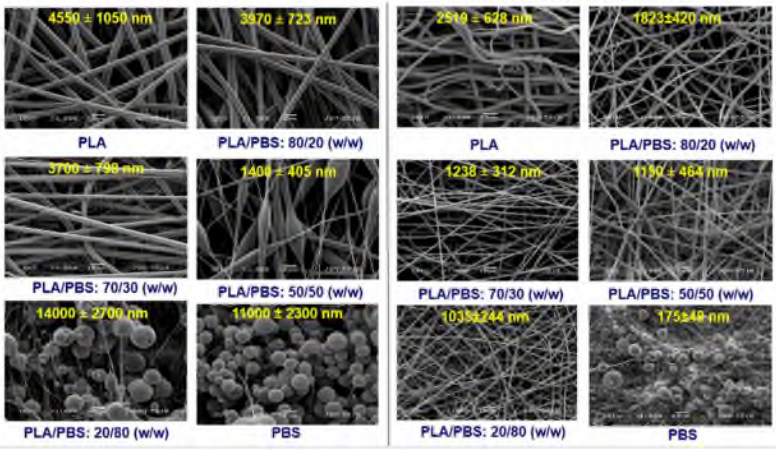
potassium 5-nitro-8-quinolate (K5N8Q)

CHARACTERIZATION OF FIBROUS MATERIALS

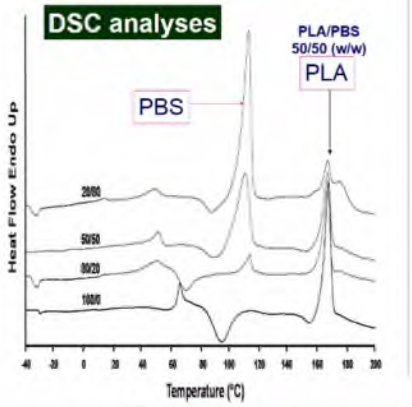
SEM

Solvent: CH_2Cl_2

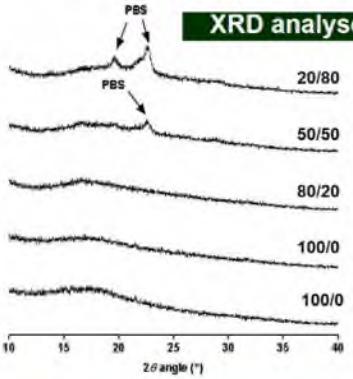
Solvents: CH_2Cl_2/C_2H_5OH



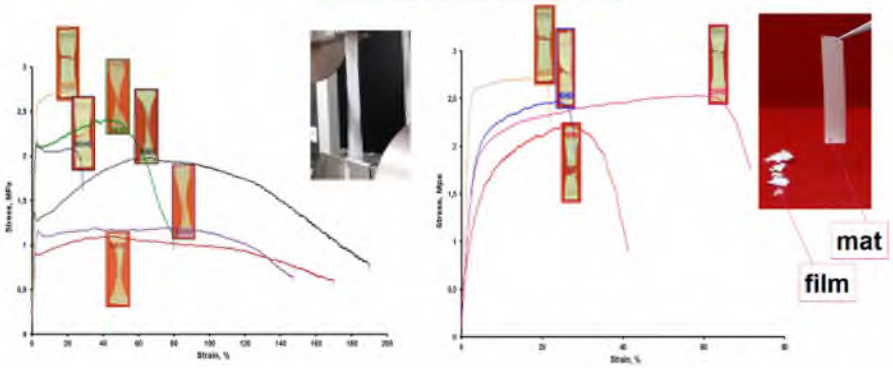
DSC analyses



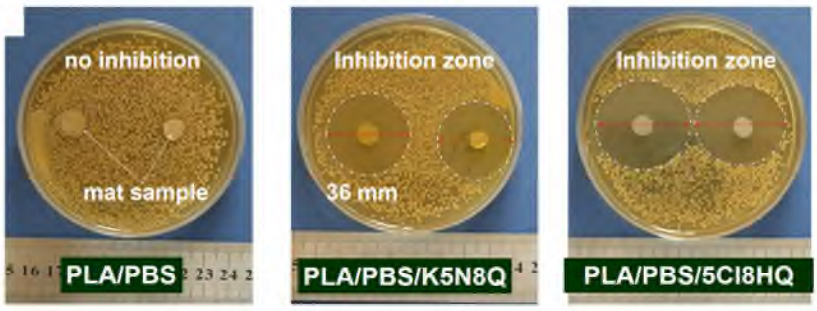
XRD analyses



Mechanical testing



Microbiological tests (*S. aureus*)



CONCLUSION

Optimal conditions for the fabrication of fibrous materials from PBS and PLA were found. The prepared new electrospun non-woven textiles are appropriate for application for example as active degradable packaging materials or as drug-loaded wound dressings.

[1] Stoyanova N., Mincheva R., Paneva D., Manolova N., Dubois Ph., Rashkov I. , *European Polymer Journal* 2012; 48: 1965–1975

*contact: rashkov@polymer.bas.bg

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N.S. acknowledges the OP-HRD Grant BG051PO001-3.3.06-006 of the European Social Fund as well as to POLINNOVA 7FP REGPOT-2012-2013-1 Grant 316086

ПОСТЕР № 21

Стерично стабилизиране на липозоми чрез новосинтезирани полимери на основата на полиглицидол, конюгиран с липидо-подобна котва

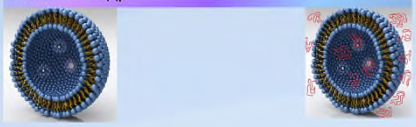
[a]Павел Бакърджиев, [a]Станислав Рангелов , [b]Деница Момекова

[a]Институт по полимери, Българска академия на науките, 1113-София, pavettoo@abv.bg
[b]Катедра "Технология на лекарствените средства с биофармация", Фармацевтичен факултет, Медицински университет-София

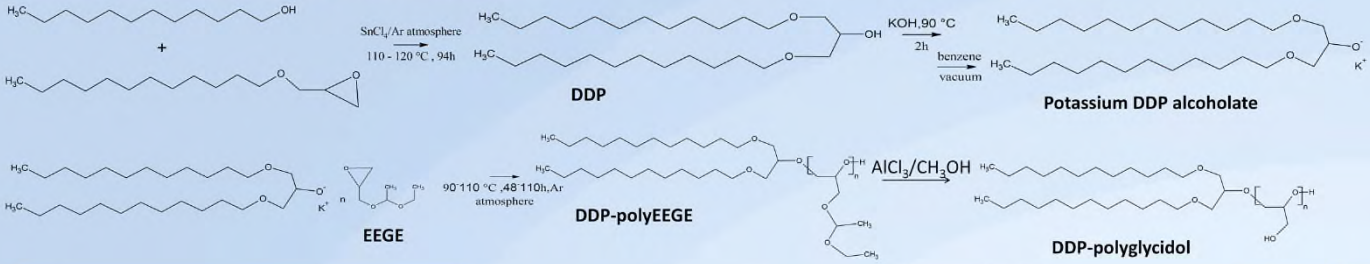
Въведение

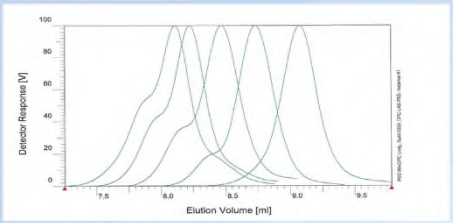
Липозомите са структури, изградени от фосфолипидни молекули, формиращи непрекъснат двоен липиден слой, заграждащ част от дисперсната среда. Строежът им позволява включването както на хидрофилни така и на хидрофобни лекарства, а наличието на мембрана ограничава контакта на лекарственото вещество с околните тъкани.
Конвенционалните липозоми са нестабилни структури, с кратък плазмен полуживот, поради взаимодействието им с клетки на мононуклеарната фагоцитираща система.Поради тази причина с цел по-голяма *in vivo* устойчивост се разработват т.нар. "stealth" липозоми, с включен в мембраната липид или липидо-подобно вещество, конюгирано с хидрофилен и биосъвместим полимер.Полиетилен гликолът(PEG) е най-често използваният за тази цел полимер. Настоящото проучване има за цел да установи потенциала на полиглицидола, като алтернатива на PEG при стеричното стабилизиране на DPPC/CHOLESTEROL липозоми.

Схема на униламеларна липозома: В ляво – конвенционална липозома и в дясно – "stealth"-липозома.В червен цвят са отбелязани веригите PEG.Наличието на полимерни вериги позволява функционализирането им с различни субстрати, осигуряващи насочено действие на липозомите в организма, като например антитела, пептиди, витамини и др.

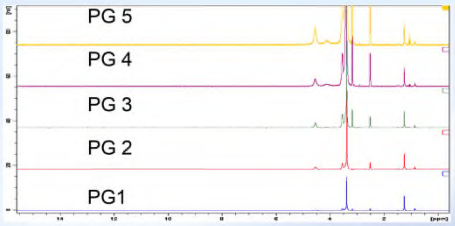


Синтез и охарактеризиране на полимерите



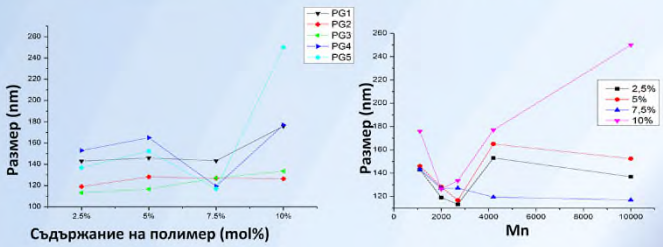


DDP-polyglycidol	Mn(nmr)	PDI (GPC)
n = 8 (PG 1)	1100	1.44
n = 20 (PG 2)	2000	1.35
n = 30 (PG 3)	2700	1.39
n = 50 (PG 4)	4200	1.38
n = 130 (PG 5)	10000	1.44

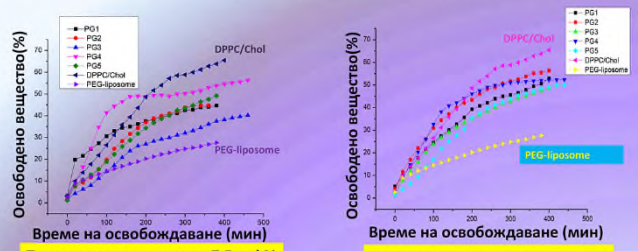


Получаване и охарактеризиране на DPPC/CHOL/DDP-polyglycidol липозоми

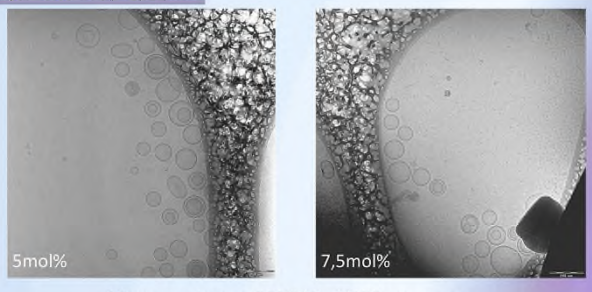
Размери, определени чрез динамично светлоразсейване



In vitro освобождаване на 5(6)-карбоксифлуоресцеин



Cryo-TEM микрографии



Микрографии на DPPC/Chol/PG3 липозоми

Заключение

Успешно бе проведена анионна полимеризация с отваряне на пръстен на защитен глицидол, инициирана от алкохолат на DDP в ролята на липофилна котва.Синтезите бяха извършени **в маса**, чрез което бе избегната употребата на органични разтворители.Бяха получени серия от полимери с различна молекулна маса, чиито свойства да придават стерична стабилност на липозоми бе проучена. От информацията, получена от освобождаването на заредени с флуоресцентно багрило липозоми, се съди за стабилизиращ ефект на новосинтезираните полимери.
Бъдещи *In vivo* експерименти ще хвърлят светлина върху потенциалния "stealth" ефект и ще внесат допълнителна информация относно кинетиката на липозомите в организма.

Благодарности
Авторите изказват своите благодарности на проекти POLINNOVA и Фонд научни изследвания ДО Б01/25 за финансовата подкрепа

SURFACE MODIFICATION OF SILICON COATINGS WITH AMPHIPHILIC BLOCK COPOLYMERS AND STUDY OF THEIR ADHESION PROPERTIES

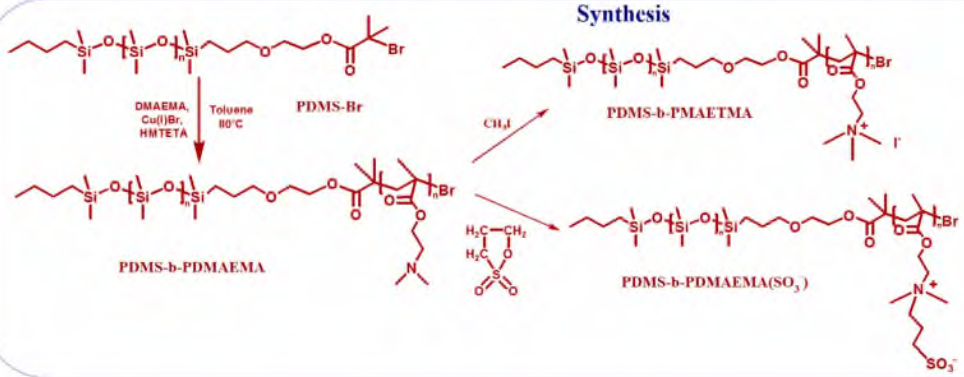
Radostina Kalinova[1‡], Chinh Ngo [2], Elise Hennebert[3], Rosica Mincheva[1], Philippe Leclére[2], Patrick Flammang[3], Roberto Lazzaroni[2], Philippe Dubois[1]

[1]Laboratory of Polymeric and Composite Materials, [2]Laboratory for Chemistry of Novel Materials, Center for Innovation and Research in Materials and Polymers (CIRMAP), University of Mons-UMONS, 20, Place du Parc, 7000 Mons, Belgium
[3]Laboratory of Marine Biology, University of Mons-UMONS, 20, Place du Parc, 7000 Mons, Belgium

Introduction

Nature has been developing adhesives for millions of years, mankind for just a few thousands of years. For this reason it is worth having a closer look at what nature does and how we can develop bio-inspired adhesives for technical and medical applications. One important advantage of nearly all kinds of bioadhesives is binding in the presence of water or even under water due to their special chemical composition, which is something difficult to realize with a technical adhesive. Our attempts are focused on producing adhesives by modification of silicon coatings with model amphiphilic block copolymers and measuring their adhesion.

Synthesis



First α-bromo PDMS (Br-PDMS) was used for atom transfer radical polymerization (ATRP) of DMAEMA monomer with copper (I) bromide (CuBr) ligated with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as catalytic complex. The obtained PDMS-b-PDMAEMA copolymers with various lengths of the PDMAEMA block were successfully quaternized and betainized further by methyl iodide and 1,3-propane sultone.

Preparation and characterization of silicon surface coated with amphiphilic block copolymers

The resulting diblock copolymers were dispersed in a PDMS matrix using a dry method and were considered for tuning the surface properties of these condensation-curing silicone coatings. The surface composition of the coatings before and after immersion in water was analyzed via X-ray photoelectron spectroscopy (XPS) and their wettability was assessed by contact angle and surface tension measurements.

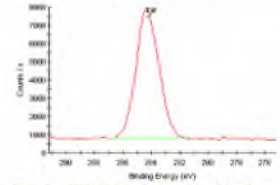


Figure 1. XPS spectrum of PDMS-b-PDMAEMA filled coatings before immersion in water

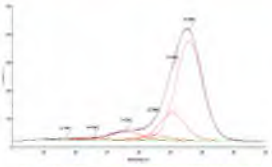


Figure 2. XPS spectrum PDMS-b-PDMAEMA filled coatings after immersion in water

XPS spectra show the presence of the block copolymer on the coatings surface after immersion in water due to the surface reorganization.

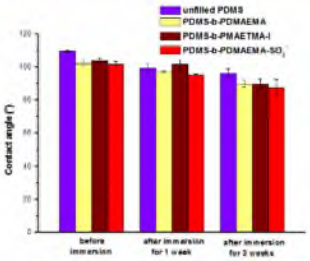


Figure 3. Static contact angle of unfilled PDMS and block copolymer filled coatings

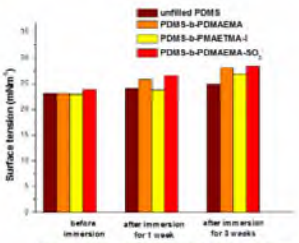


Figure 4. Surface tension of unfilled PDMS and block copolymer filled coatings

The decrease in hydrophobicity and increase of the surface tension of block copolymer-modified coatings was observed after immersion in water, evidencing again the presence of block copolymers on the coating surfaces.

Adhesion measurements

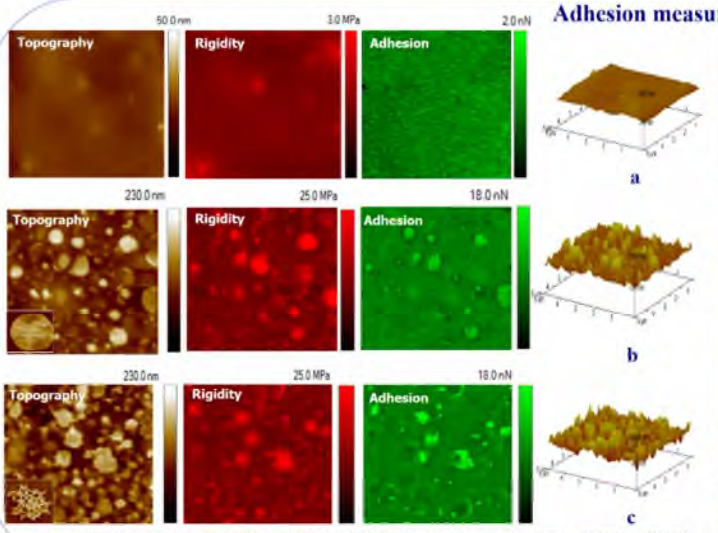


Figure 5: PFT AFM images of a) unfilled PDMS, b) PDMS-b-PDMAEMA filled coatings before immersion in water, c) PDMS-b-PDMAEMA filled coatings after immersion in water

Films	Surface roughness: R_q (nm)	Rigidity (MPa)	Adhesion (nN)
Unfilled PDMS	1.17	0.8	0.8
PDMS filled with PDMS-b-PDMAEMA before immersion	17.5	23.8	8.9
PDMS filled with PDMS-b-PDMAEMA after immersion in water	24.8	16.8	13.7

New morphology of PDMS-b-PDMAEMA filled coatings after immersion in water (Figure 6) and increase in the surface roughness and adhesion values (Table 1) was evidenced from AFM measurements.

Table 2. Average pulling force measured for PDMS coatings

Silicon coating \ Average pulling force (N)	Before immersion	After immersion
$PDMS_{130}$-b-$PDMAEMA_{124}$	No adhesion	0.068±0.002
$PDMS_{130}$-b-$PDMAEMA_{124}(SO_3)_3$	No adhesion	0.077±0.002
Unfilled PDMS	No adhesion	No adhesion

The adhesion of mussels was measured only in the case of block copolymer filled coating after immersion in water.

Conclusion:

Silicon coatings filled with amphiphilic block copolymers were successfully prepared. The coatings surface reorganization after immersion in water was evidenced by the change in their wettability and surface properties. The performed adhesion measurements highlighted the increase in the adhesion under water.

‡ *Present address : Acad. G. Bonchev Str., block 103-A, BG - 1113 Sofia, Bulgaria*

What is the effect of catalysts for metathesis and other transformation?

Silvia Dimova[1], Katerina Zaharieva[2], Christo Jossifov[1], Zara Cherkezova-Zheleva[2], Boris Kunev[2]

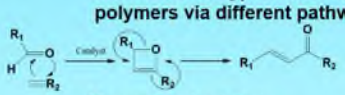
[1]Institute of Polymers, Bulgarian Academy of Sciences, bl. 103A, Bulgaria, e-mail: dimova@polymers.bas.bg
[2]Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., bl.11, 1113 Sofia, Bulgaria, e-mail: zaharieva@ic.bas.bg

AIM

The main direction in our recent summarized research is to investigate effect of different catalytic systems and synthesis conditions for preparation of polymers.

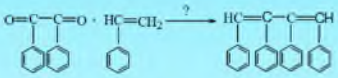
INTRODUCTION

The metathesis is a widely used synthetic method, and is a effective technique for different chemical structures by formation of a new carbon-carbon bonds. These chemical reactions can be used for polymerization of molecules or coupling, breaking, ring-closing, ring-opening. Under the influence of various types of catalysts WCl6, AgSbF6, and nickel ferrite type materials NixFe3-xO4 (x=0.25,0.5,1) some α, β carbonyl compounds can be transformed into polymers via different pathways.



Alkyne carbonyl metathesis

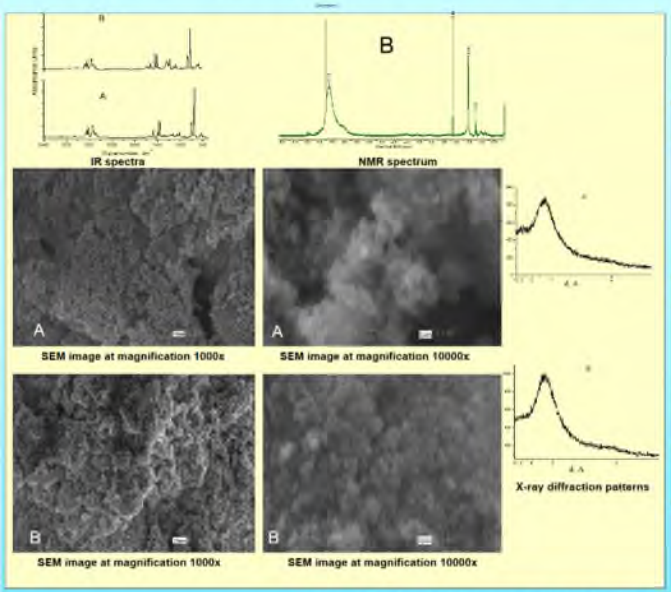
EXPERIMENTAL

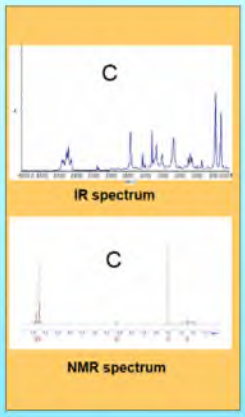


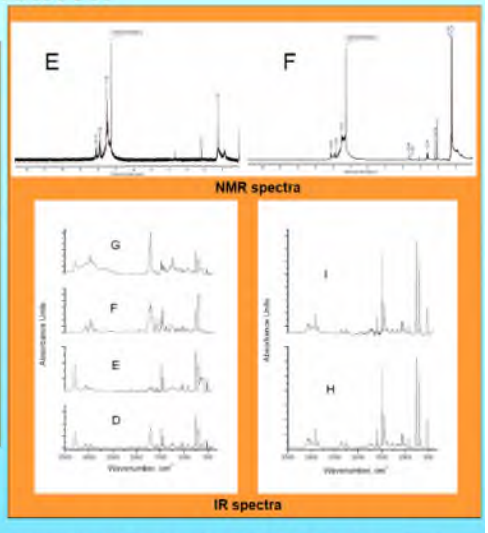
Monomer	Comonomer	Catalyst	Temperature, °C	Time, h	Product
Benzil	Styrene	WCl_6	90	3	Polystyrene (A)
Benzil	Styrene	WCl_6	90	3	Polystyrene (B)
phenylpropyne	isobutyraldehyde	$AgSbF_6$	70	24	polyacetylenes with carbonyl end group (C)
1-phenylacetylene	isobutyraldehyde	$Ni_{0.25}Fe_{2.75}O_4$	80	4	polyphenylacetylenes with a carbonyl end group (D)
1-phenylacetylene	isobutyraldehyde	$Ni_{0.5}Fe_{2.5}O_4$	80	4	polyphenylacetylenes with a carbonyl end group (E)
1-phenylacetylene	isobutyraldehyde	$Ni_{0.5}Fe_{2.5}O_4$	80	24	polyphenylacetylenes with a carbonyl end group (F)
1-phenylacetylene	isobutyraldehyde	$NiFe_2O_4$	80	4	polyphenylacetylenes with a carbonyl end group (G)
1-phenyl-1-propyne	isobutyraldehyde	$Ni_{0.25}Fe_{2.75}O_4$	80	4	polyphenylacetylenes with an olefin end group (H)
1-phenyl-1-propyne	isobutyraldehyde	$Ni_{0.5}Fe_{2.5}O_4$	80	4	polyphenylacetylenes with an olefin end group (I)

Experimental conditions:
Monomer: comonomer: catalyst = 1mol : 2mol : 1mol / benzil : styrene : WCl_6; solvent - Chlorbenzene
Monomer: comonomer: catalyst = 0.080mmol : 0.011mmol : 0.0011μmol / 1-phenyl-1-propyne/1-phenylacetylene : isobutyraldehyde : $AgSbF_6$; solvent -1,2- Dichlorethane
Monomer: comonomer: catalyst = 0.007mmol : 0.005mmol : 0.0001mmol / 1-phenyl-1-propyne/1-phenylacetylene : isobutyraldehyde : $Ni_xFe_{3-x}O_4$ (x=0.25,0.5,1); solvent-1,2- Dichlorethane

CHARACTERIZATION







CONCLUSION

- **The effect of different catalysts as WCl_6, $AgSbF_6$, nickel ferrite materials $Ni_xFe_{3-x}O_4$ (x=0.25,0.5,1) and synthesis conditions on the preparation of different chemical architectures are successfully studied.**
- **The WCl_6 catalyst promotes homo- and co-polymerization of styrene and benzil.**
- **The investigations using as catalysts $AgSbF_6$, and nickel ferrite type materials $Ni_xFe_{3-x}O_4$ (x=0.25,0.5,1) show the presence of oligomers with low molecule weight and polyphenylacetylenes segments.**
- **The obtained products expected to have photoluminescent and photoelectrical properties and in the future will be investigated.**

ACKNOWLEDGEMENTS

S. Dimova thanks for the financial support of POLINNOVA funded by the European Commission under the Seventh Framework Programme. The authors from IC-BAS acknowledge the sponsorship of Bulgarian National Science Fund under Project DFNI-E01/7/2012. We are grateful to Dr. K Starbova and Dr. N. Starbov for expert opinion and help about SEM investigations.

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ПОСТЕР № 24

Четвърта постерна сесия
"Младите учени в света на полимерите"

pH-чувствителни супер-макропорести крогелове на основата на фотоомрежени хитозан и хидроксиетилцелулоза

Веселина Стойнева[a], Петър Петров[a]

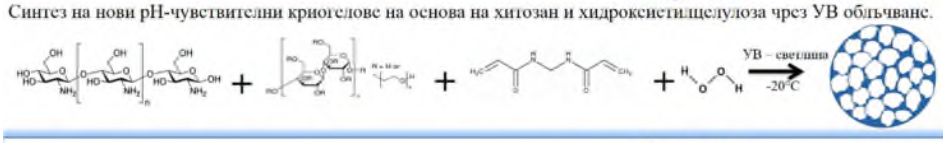
[a] Институт по полимери, Българска академия на науките ; e-mail: vstoyneva@polymer.bas.bg

Увод

Супер-макропоресттите криогелове са интересен клас полимерни хидрогелове поради уникалната си хетерогенна пореста структура, която значително подобрява сорбционните им свойства и позволява безпрепятствено проникване на разтворени вещества, нано- и дори микро-частици. Освен това pH-чувствителните супер-макропорести криогелове могат да претърпят обратим фазов преход при промяна на pH на средата. Целта на представеното изследване е да се синтезират нови супер-макропорести криогелове от биоразградими полимери от възобновяеми източници с добри адхезивни свойства.

Стратегия

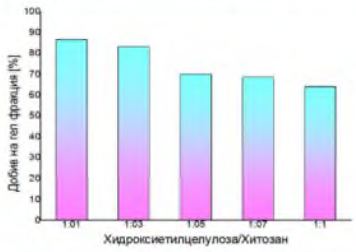
Синтез на нови pH-чувствителни криогелове на основа на хитозан и хидроксиетилцелулоза чрез УВ облъчване.



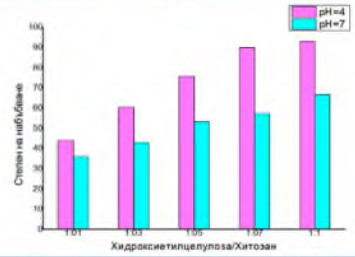
Криогелове се образуват при замразяване на хомогенен воден разтвор на хитозан, хидроксиетилцелулоза, омрежващ агент и инициатор при pH 4, при температура минус 20° C, облъчване с УВ светлина за 2 минути с доза 5,7 J/cm² . min, и последващо размразяване.

Резултати

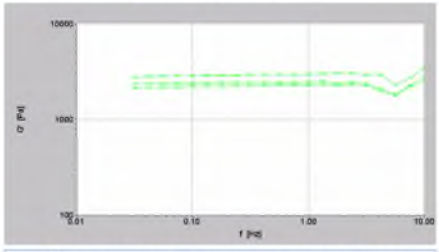
1. Изследване ефекта на масовото съотношение



С увеличаване съдържанието на хитозан, добива на гел фракция леко намалява, но всички получени криогелове са монолитни и не се разпадат в неутрална и кисела вода.

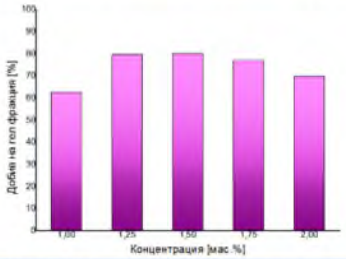


С увеличаване съдържанието на хитозан се достига до по-висока степен на набъбване на получените криогелове в кисела среда.

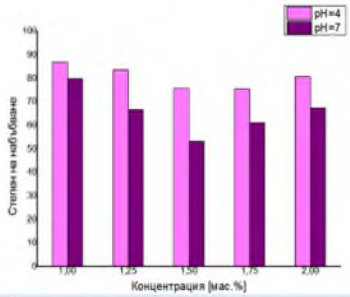


Модулът на еластичност е определен след измерване на 3 пробни тела от една и съща система

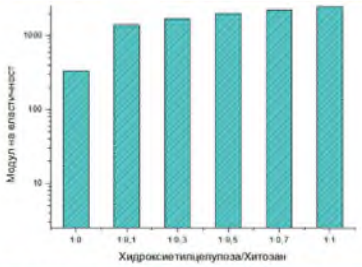
2. Изследване ефекта на полимерната концентрация



Най-висок добив на гел фракция се постига при изходна концентрация на разтвора 1,5 мас. %

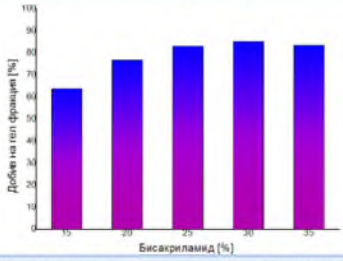


Включването на хитозан променя степента на набъбване на криогеловете при различно pH на средата.

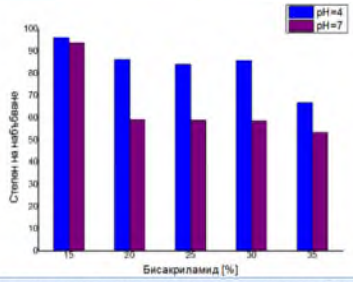


С увеличаване съдържанието на хитозан се увеличава и модула на еластичност на криогеловете.

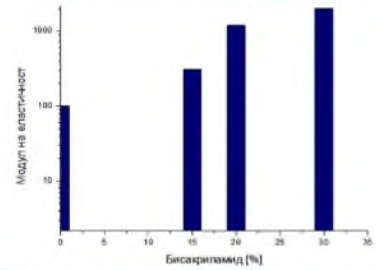
3. Изследване съдържанието на омрежващ агент за омрежваща ефективност



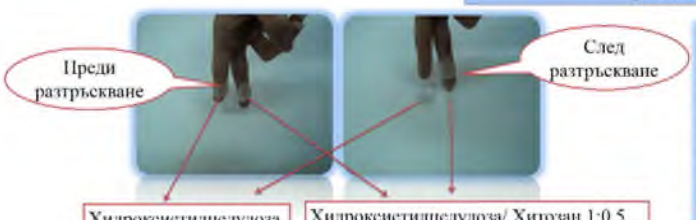
Включването на бисакриламид в полимерната мрежа увеличава добива на гел фракция на получените криогеловете.



С увеличаване процентното съдържание на бисакриламид включен в полимерната мрежа води до намаляване на степента на набъбване на криогеловете.



Включването на бисакриламид в полимерната мрежа значително увеличава модула на еластичност на криогеловете.



Включването на хитозан в криогеловете повишава адхезивните им свойства

Заключение

За първи път успешно са получени супер-макропорести криогелове от смес на хидроксиетилцелулоза и хитозан, чрез фотохимично омрежване в замразени водни системи. Включването на хитозан в полимерната мрежа придава pH-чувствителност на материалите, повишава степента на набъбване и модула на еластичност.

Благодарности: Настоящето изследване е финансирано от Фонд Научни Изследвания (проект UNION; ДЦВП 02/2 - 2009) и Европейската комисия (проект POLINNOVA)

Synthesis and aqueous solution properties of PEO-PnBA and PEO-PnBA-PAA block copolymers

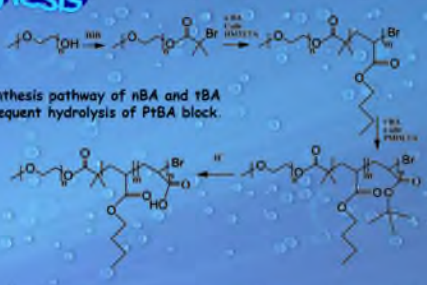
Yana Peneva-Stoyanova, Petar D. Petrov, Krassimira Yoncheva, Pavlina Mokreva, Spiro Konstantinov, Juan M. Irache, and Axel H.E. Müller

Introduction

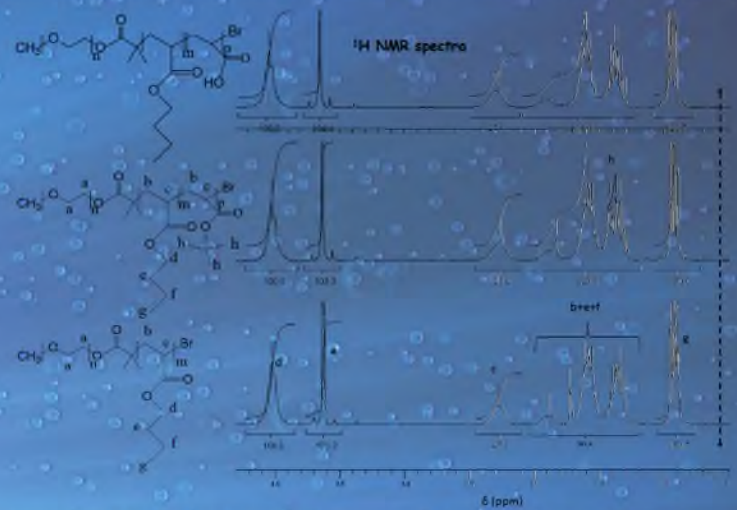
PEO-PPO-PEO triblock copolymers are among the most extensively studied copolymers for development of drug and gene delivery systems. In water they form spontaneously core-shell micelles which are in dynamic equilibrium with molecularly dissolved copolymer chains, that's why they are very sensitive to changes in concentration and temperature and may dissociate very fast upon injection in the blood stream. The so-called frozen polymer aggregates are able to maintain their size and morphology upon dilution at very low concentration and can be considered as promising long-circulating drug delivery systems.

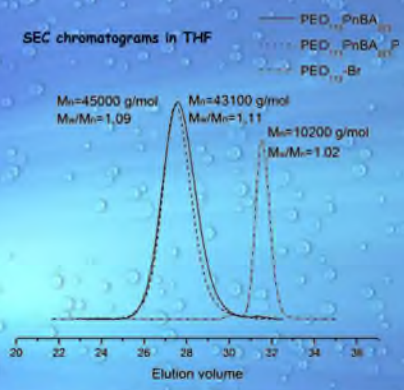
In this study novel amphiphilic PEO-PnBA-PAA triblock terpolymers are synthesized and their aqueous solution properties are investigated. The length of PEO block (DP_n=113) was kept longer than that of PAA block (DP_n=10-17).

Synthesis



ATRP synthesis pathway of nBA and tBA and subsequent hydrolysis of PtBA block.





Target composition	Calculated copolymer composition $^{1H\ NMR}$	[M]:[I]:[Cu(I)]:[L]	Reaction temperature (°C)	Reaction time (h)	Monomer conversion/ hydrolysis $^{1H\ NMR}$ (%)
$PEO_{113}PnBA_{160}$	$PEO_{113}PnBA_{163}$	400:1:0.5:0.5	70	22	39
$PEO_{113}PnBA_{244}$	$PEO_{113}PnBA_{223}$	610:1:0.5:0.5	70	30	38
$PEO_{113}PnBA_{163}PtBA_{15}$	$PEO_{113}PnBA_{163}PtBA_{12}$	15:1:1:1	50	73	80
$PEO_{113}PnBA_{163}PAA_{12}$	$PEO_{113}PnBA_{163}PAA_{12}$	-	20	65	> 99*
$PEO_{113}PnBA_{223}PtBA_{10}$	$PEO_{113}PnBA_{223}PtBA_{10}$	20:1:1:1	50	51	50
$PEO_{113}PnBA_{223}PtBA_{20}$	$PEO_{113}PnBA_{223}PtBA_{17}$	40:1:1:1	50	71	42
$PEO_{113}PnBA_{223}PAA_{10}$	$PEO_{113}PnBA_{223}PAA_{10}$	-	20	60	> 99*
$PEO_{113}PnBA_{223}PAA_{17}$	$PEO_{113}PnBA_{223}PAA_{17}$	-	20	60	> 99*

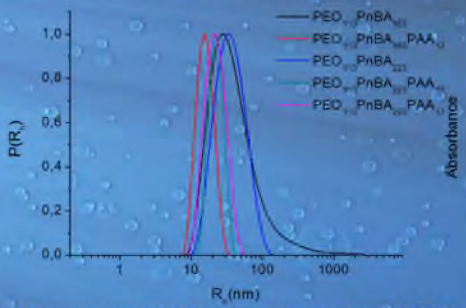
Experimental conditions and composition of PEO-PnBA-PAA triblock terpolymers, PEO-PnBA diblock copolymer and PEO-PnBA-PtBA triblock terpolymer precursors synthesized by ATRP

Aqueous solution properties

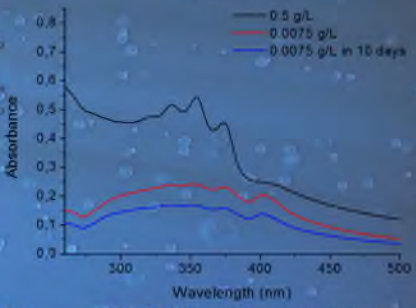
Copolymer	$Mn^{1H\ NMR}$ (g/mol)	Mn^{GPC} (g/mol)	PDI^{GPC}	R_h^{90} (nm)	PDI^{DLS}
$PEO_{113}PnBA_{163}$	26000	37600	1.16	27	0.30
$PEO_{113}PnBA_{163}PtBA_{12}$	27500	38100	1.11	-	-
$PEO_{113}PnBA_{163}PAA_{12}$	26800	-	-	16	0.19
$PEO_{113}PnBA_{223}$	33800	43100	1.11	35	0.24
$PEO_{113}PnBA_{223}PtBA_{10}$	34900	44450	1.10	-	-
$PEO_{113}PnBA_{223}PtBA_{15}$	35500	45000	1.09	-	-
$PEO_{113}PnBA_{223}PAA_{10}$	34300	-	-	22	0.18
$PEO_{113}PnBA_{223}PAA_{15}$	34700	-	-	22	0.18

Molecular characteristics of PEO-PnBA-PAA triblock terpolymers, PEO-PnBA diblock copolymer and PEO-PnBA-PtBA triblock terpolymer precursors synthesized by ATRP

Dynamic light scattering



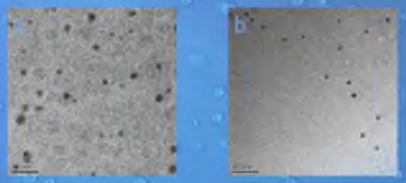
UV-vis absorption spectra



Diblock copolymers and triblock terpolymers comprising longer PnBA block form larger micelles as compared to these with shorter PnBA block. The existence of very short PAA blocks in the macromolecules of terpolymers definitely leads to a decrease of the micellar size and size distribution.

PEO-PnBA-PAA micelles are resistant upon severe dilution and do not dissociate quickly, which is typical for kinetically frozen systems.

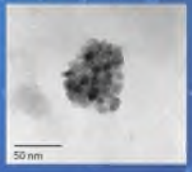
Cryo-TEM



Schematic illustration of "crew-cut" micelles

Silver nanoparticles incorporation

To illustrate the additional functionality of PEO-PnBA-PAA micelles, imparted by incorporation of PAA chains, template-assisted formation of AgNPs was performed. Spherical nanoparticles with dimension about 5-10 nm seem to be arranged in the area occupied by the micelle.



Conclusions

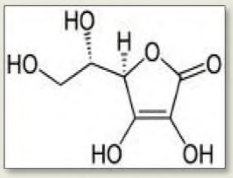
PEO-PnBA-PAA triblock terpolymers with controlled composition and narrow molar mass distribution formed defined spherical "crew-cut" micelles in aqueous media with the aid of co-solvent. As DP_n of PEO (113 units) exceeded significantly DP_n of PAA (10-17 units) block, formation of three-layer micellar structure comprising a soft PnBA core, a PEO/PAA middle layer, and a PEO outer layer is suggested. The existence of third PAA block resulted in formation of micelles with smaller size and narrower size distribution as compared to the PEO-PnBA micelles. The introduction of PAA chains imparts also additional functionality to the system as evidenced by the synthesis of AgNP within the micelle templates. The type and length of the hydrophobic block (PnBA: DP_n<163 or 223) determined an excellent stability of micellar structures upon severe dilution, which in combination with the ability of PEO-PnBA-PAA micelles to release drug without burst effect makes them promising candidate for long-circulation drug delivery systems. The potential of PEO-PnBA-PAA micelles as vehicles of both anti-angiogenic drug and AgNPs could be further explored for achieving a synergistic effect at the inhibition of tumor growth.

Acknowledgements: The financial support of the National Science Fund of Bulgaria (DO1-25/2012) and the European Commission (Polinnova) is gratefully acknowledged.

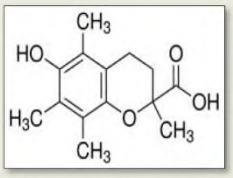
ПОСТЕР № 26

INFLUENCE OF LIPID- AND WATER- SOLUBLE ANTIOXIDANTS ON OXIDATIVE TOXIC EFFECTS OF MADOPAR IN EXPERIMENTAL MODELS OF MICE - EPR STUDY

G. Nikolova, D. Ivanova, B. Grigorov, Y. Karamalakova, E. Georgieva, A. Zheleva, V.Gadjeva
Department Chemistry and Biochemistry, Medical Faculty, Trakia University, 11 Armeiska Str., 6000 Stara Zagora, Bulgaria



a Ascorbic acid



b Trolox –water solubl analog of vit. E

Figure 1. Water soluble antioxidants - Ascorbic acid and Trolox

Figure 2. Lipid- soluble antioxidants *Rosa Damascena Mill* and *Lavendula angustifolia Mill*

INTRODUCTION

Madopar is a drug used for treatment of patients suffering from Parkinson disease. There is increased data provides enough evidences confirming that long–term Madopar administration increased oxidative toxic effect.

A lot of studies have been shown that free radical scavengers and antioxidants are useful in protecting against oxidative toxicity from drug. Moreover, it is known that antioxidants, such as Vit E, Vit C may prevented lipid peroxidation and cell destruction.

The aim of this study was to investigate the possible protective role of Vit E, Vit. C, Rose oil and Lavender oil in mice acutely treated with Madopar.

MATERIALS and METHODS

White male mice divided into 6 groups, were used. Control group and the group with Madopar (combination of levodopa and benserazide) received two i.p. injections of either saline or a combination of Levodopa (100mg/kg) and Benserazide (10mg/kg). The second injection was given after 45 minutes. Other four groups respectively were pretreated with 400 mg/kg of rose oil (*Rosa Damascena Mill*), lavender oil (*Lavendula angustifolia Mill*), Ascorbic acid or Trolox, i.p., and one hour later, they received two i.p. injections of Levodopa (100mg/kg) and Benserazide (10mg/kg). All animals were sacrificed 30 min after the second injection.

The levels of lipid radicals, Asc• and NO• were determined by EPR spectroscopy methods at room temperature on an X-band EMX ^{micro} spectrometer, Bruker, Germany in brain homogenates of experimental mice.

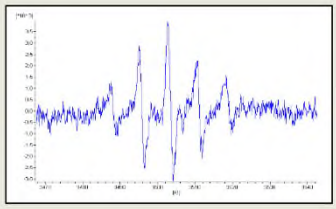


Figure 3. EPR spectra of NO radical in brain homogenate

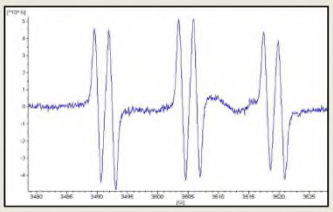


Figure 4. EPR spectra of Lipid radicals in brain homogenate

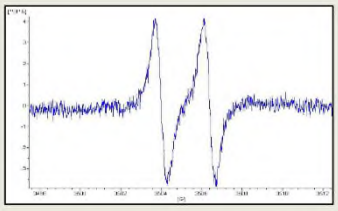


Figure 5. EPR spectra of Asc• in brain homogenate

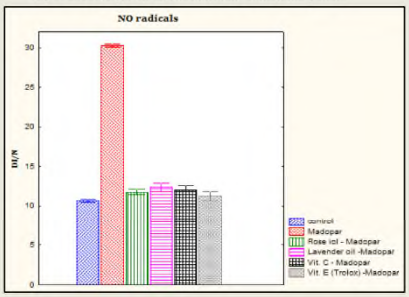


Figure 6. The levels of NO radicals in brain homogenates

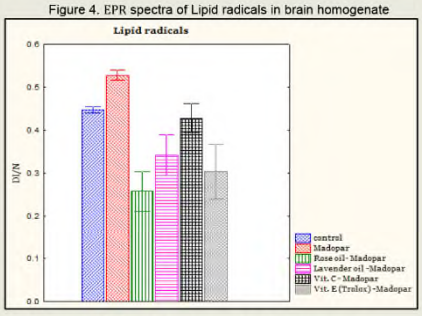


Figure 7. The levels of Lipid radicals in brain homogenates

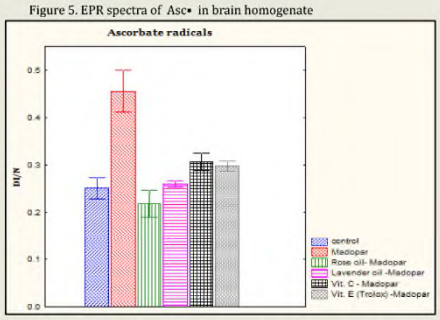


Figure 8. The levels of Ascorbate radicals in brain homogenates

Results

Increased levels of Asc•, NO• and Lipid radicals were established in the brain homogenate of mice treated only with Madopar, which could be associated with L-dopa metabolism and ROS generation. All other groups pre-treated with antioxidants before Madopar administration showed decreased of the levels of oxidative stress parameters with values closed to the controls, which is due on the antioxidants role in scavenging of free oxygen/nitrogen radicals.

Conclusions

By the present study we reported higher levels of oxidative stress markers in mice treated with Madopar, and protective role of investigated lipid and water soluble antioxidants.

Keywords: Lipid radicals; Ascorbate radicals, NO radicals, EPR.

Acknowledgements:
This work was supported by the scientific project № 4/2013 of MF, Trakia University and project № BG051PO001-3.3.06-0006. Authors thanks the European Social Fund, Structural Funds, Operational Programme "Human Resources Development" for financial support in frame of Grant BG051PO001-3.3.06-0006

E-mail: vgadjeva@mf.uni-sz.bg
gnikolova@mf.uni-sz.bg

BIODISTRIBUTION OF SYNTHETIC AND NATURAL ANTIOXIDANTS IN ORGANS OF EXPERIMENTAL MICE: COMPARATIVE EPR INVESTIGATION

Y. Karamalakova *, G. Nikolova*, R. Kumar**, R. Arora**, R.K. Sharma**, E. Georgieva*, A. Zheleva*, V. Gadjeva*

Department Chemistry and Biochemistry, Medical Faculty, Trakia University, 11 Armeiska Str., 6000 Stara Zagora, Bulgaria

****Institute of Nuclear Medicine and Allied Sciences, INMAS, Delhi- 110054 , India**

Introduction Electron paramagnetic resonance (EPR) spectroscopy is a proper method for investigation of synthetic and natural antioxidants, organ distribution, and free radicals in biological systems, including the *ex vivo* tissue homogenates and blood samples. This technique provides unique details that allow us to measure and represent processes of the metabolism of free radicals, the reactive oxygen species (ROS), organ/tissue oxygenation and drugs location and nitrous oxide production (RNS) in the normal physiology. Formerly, for natural antioxidants (SQGD and Psoralea *Corilifolia Linn.)* were established that possessed high radio protective effect against gamma radiation at *in vivo* models and well expressed radical scavenging capacity of stable radical 1,1-diphenyl-2-picrylhydrazyl(DPPH) The spin-labeled analogues (SLENU and SLCNUgly) of the anticancer drug Lomustine [1-(2-chloroethyl)-3-cyclohexyl-1 nitrosourea] were synthesized, using a substitution of the cyclohexyl part with nitroxyl spin-labeled part. The compounds exhibited good antioxidant properties, good SSA, *in vivo* lower general toxicity and higher antimelanomic effect against B16 melanoma. In the present study, we would like to introduce, evaluate and compare the EPR pharmacokinetic/ biodistribution studies in organs of synthetic drugs and natural antioxidants.

Materials and methods Synthetic nitroxyl- labeled nitrozoureas SLENU and SlCNU gly (Fig 1) was previously synthesized in the Trakia University, Bulgaria. Natural antioxidants SQGD (Bacillus sp. INM-1, MTCC No.1026) and Psoralea Colirifolia Linn. (Fig 2) were deposited at INMAS, India as reference. Biodistribution study of drugs (a.i.p./ dose 40 mg/kg) in organ homogenates (lungs, liver, spleen, brain, kidneys, pancreas) and blood was evaluated in male albino non-inbred mice (35- 40 g body weight, normal diet). Animals were decapitated at 10, 30, 60, 90 min/ 4h, 24h and dissected. The free streaming blood was collected into heparinized tubes containing PBS (pH =7-7.4). Tissues from organs were collected and processed immediately. Samples were weighed and homogenized in PBS (10% w/v) and centrifuged at 2000 g for 15 min. Supernatants were collected and the concentration of antioxidants were evaluated by EPR spectroscopy. Before measuring, the nitroxil- labeled concentration, the samples were deoxidized by $K_3[Fe(CN_6)]$, because of the fast reduction of the nitroxide function (10-20 min) in the tissues.

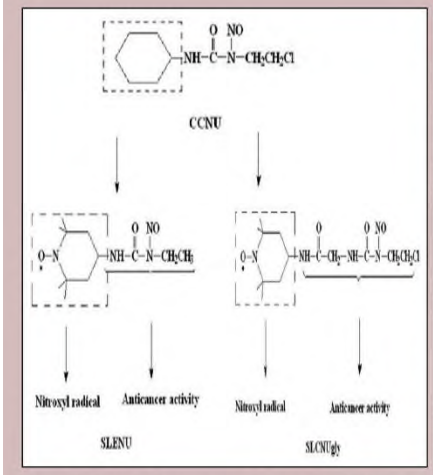


Figure 1. Chemical structures of Lomustine (CCNU) and nitroxyl- labeled analogues SLENU and SLCNU gly.

Results The blood clearance studies of free drug conducted showed that the half-life of the drug was greater than the drug in its free state. The maximum concentration in blood reached at 60 min- SLENU; 10 min- SLCNU gly; at 30 min- SQGD; 90 min– Psoralea Linn, after i.p. injection and almost completely observed after 4h. The spin-labeled nitrosoureas and natural antioxidants were mainly localized in the lungs, in the liver, in the pancreas and in the brain. The highest concentration of the synthetic drugs were observed in the brain (5.647 ± 1.012 a.u.) for SLENU on the 60 min and (1.2261+ 0.056 a.u.) for SLCNUglu on the 10 min. In comparision, the highest concentration of the natural drugs were observed in the brain (0.7687 ± 0.431 a.u.) for Psoralea Linn. and (0.5825 + 0.0356 a.u.) for SQGD on the 90 min. The minimum concentration of the synthetic drugs were observed in the kidneys for SLENU on the 60 min and in the spleen for SLCNUglu on the 10 min. In comparision, the minimum location of the natural drugs were observed in the blood (90 min) for Psoralea and in spleen (30 min) for SQGD (Fig 3 and Fig 4).

Conclusions

In conclusion in an ex vivo biodistribution EPR results showed that the synthetic nitrosoureas have reached a maximum concentration in all organs, within 30 minutes, whereas the natural antioxidants, the same effect begins 60 minutes after the injection.

Keywords: Synthetic and natural antioxidants, biodistribution, EPR investigations

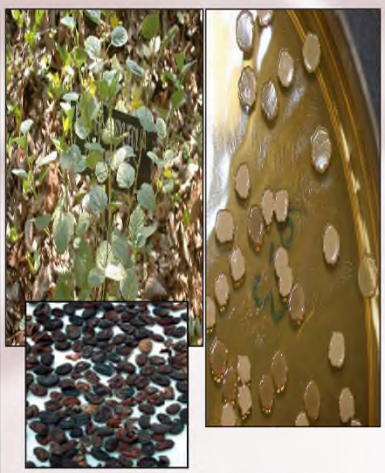


Figure 2. Pictures of Psoralea olirifolia Linn. and (Bacillus sp. INM-1, MTCC No.1026) SQGD.

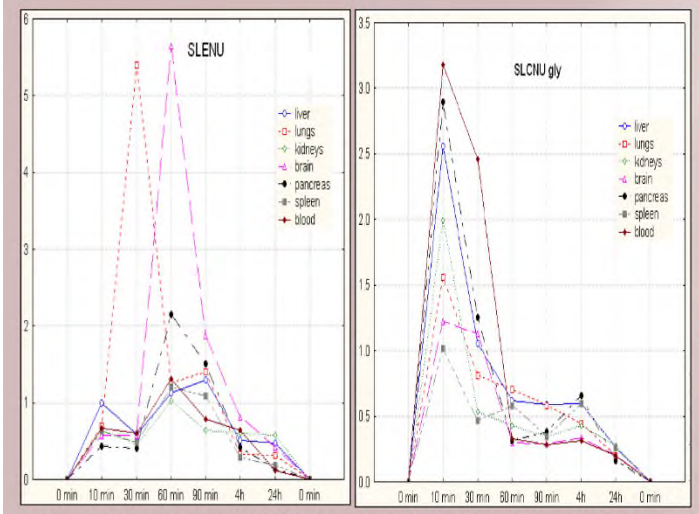


Figure 3. EPR signal intensity (DI/ N) in organs and blood of synthetic antioxidants SLENU and SLCNU gly

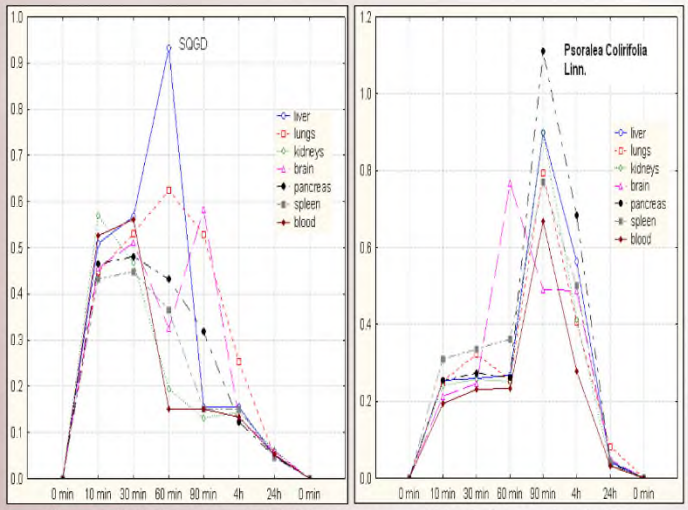


Figure 4. EPR signal intensity (DI/ N) in organs and blood of natural antioxidants SQGD and Psoralea Linn.

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Plasma-based surface functionalization of polyester/wool fabric and its interaction with acid dyes

Tarek S. Salem[1,2*], Dieter Pleul[1], Frank Simon[1]

[1] Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden (Germany)

[2] National Research Centre, El Buhouth St., Dokki, 12311 Cairo (Egypt)

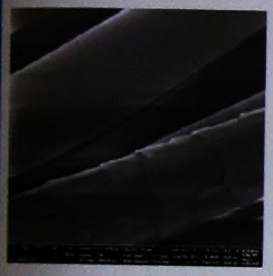
Introduction and Motivation

- Dyestuff class is limited to the chemical groups present in the fiber due to the dye/fiber interaction.
- Blends of polyester with wool represent an attempt to achieve the combination of desirable properties of both fibers. They allow the production of fabrics having good wear properties, dimensional stability, mechanical strength, abrasion resistance and attractive handle.
- One of the major problems that restrict the application of PET/wool textiles is that two classes of dyes are required for coloration to produce solid shades because of the vastly different physicochemical nature of the two components.
- Therefore, in the recent years, there has been a growing interest in the ***substrate-independent coloration*** for the materials industries , to enable chemically diverse materials to be dyed or printed by one class of dyestuffs.

Objective

- An interest in the present work is to find out appropriate engineering method, which can be further accepted by textile industries for surface functionalization of PET/wool fabrics to overcome its limited reactivity and to keep the bulk characteristics unaffected.
- Toward this goal, new synthetic route was employed to endow PET/wool fabrics with accessible and reactive primary amino groups.

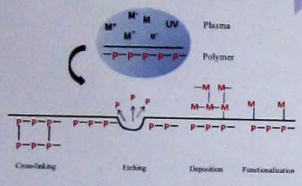
Synthetic concept

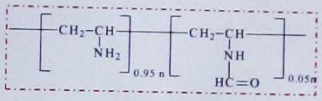


PET/wool fabric

(1) Low-Pressure oxygen plasma

(2) Adsorption of poly (vinyl amine-*co*-vinyl amide) (PVAm) from aqueous solution





Results

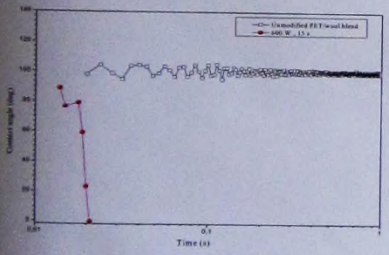


Figure 1 Contact angles of water droplets in dependence on resting time on the unmodified PET/wool fabric and oxygen plasma-modified (600 W, 15 s) PET/wool fabric. The error of each measurement is ± 2°.

Table 1 The surface elemental composition and elemental ratios determined by XPS for the unmodified PET/wool, oxygen plasma-modified (600 W, 15 s) PET/wool and PVAm-modified PET/wool fabrics obtained with C_{PVAm}= 3 wt. %.

Fabric sample	C (at %)	O (at %)	N (at %)	S (at %)	[N]:[C]	[O]:[C]	[S]:[C]
Unmodified PET/wool blend fabric	73.9	18.5	5.2	1.6	0.07	0.25	0.02
Oxygen plasma-modified PET/wool blend fabric	59.8	30.1	7.7	1.8	0.13	0.5	0.03
Modified with 3 wt.% PVAm blend fabric	70.9	15.9	11.1	1.4	0.17	0.22	0.02

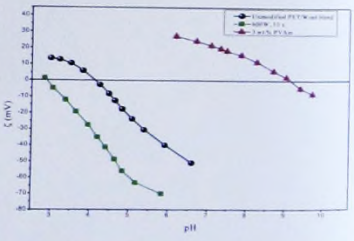


Figure 2 ζ-pH dependence for the unmodified PET/wool fabric, oxygen plasma- modified (600 W, 15s) PET/wool fabric and PVAm-modified PET/wool fabric obtained with C_{PVAm} = 3 wt. %.

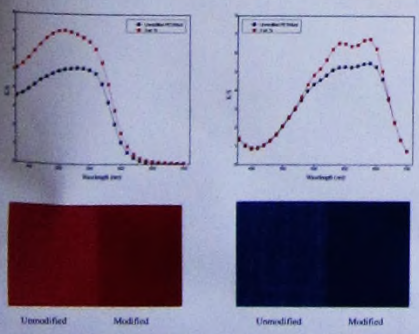


Figure 3 K/S absorption spectra of the unmodified PET/wool fabric and PVAm-modified PET/wool obtained with C_{PVAm} = 3 wt. % printed with C.I. Acid Red 18 (a) and C.I. Acid Blue 80 (b).

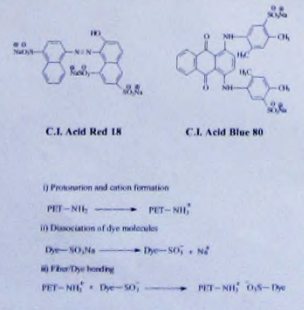


Figure 4 The binding mechanism of acid dye with modified PET fabric surface in PET/wool fabric.

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