

LOMONOSOV MOSCOW STATE UNIVERSITY

Polyelectrolyte Systems

International Summer School

Abstracts and Schedule

**Moscow, Russia
June 14 – 16, 2017**

International Summer School

Polyelectrolyte Systems

June 14–16, 2017, Lomonosov Moscow State University

Topics:

- Molecular design and synthesis
- Nanobiotechnologies and medicine
- Self-organization: experiment, theory, simulations

PARTNERS



M.V.LOMONOSOV MOSCOW STATE UNIVERSITY



**Российский
научный
фонд**

RUSSIAN SCIENCE FOUNDATION

SCIENTIFIC PROGRAM

All lectures will be held in Chemistry Department building, auditorium 446 (4th floor). Student poster session will be held in the hall near this auditorium. General registration will start on 10 a.m., June 13th, at the Second floor Central Hall. Other days registration will be available during School hours in the Committee office at North auditorium (CXA), ground (“-1”) floor.

Wednesday, June 14

11³⁰ – 11³⁵	<i>OPENING of the SCHOOL</i>
<i>Chair: Andrij Pich</i>	
11³⁵ – 12⁰⁵	Renko de Vries “Using Polyelectrolyte Complexation in de-novo Protein Design” (Netherlands)
12⁰⁵ – 12³⁵	Bharat Bhushan “Bioinspired Mechanically Durable Superliquiphilic/phobic Surfaces” (USA)
12³⁵ – 13⁰⁵	Andrey Sybachin “Complexes of anionic liposomes with cationic colloids: formation, structure and properties” (Russia)
13⁰⁵ – 14³⁰	<i>LUNCH</i>
<i>Chair: Oleg Borisov</i>	
14³⁰ – 15⁰⁰	Larisa Tsarkova “Polymer-surfactant interactions in solutions” (Russia)
15⁰⁰ – 15³⁰	Ekaterina Litmanovich “Polyelectrolyte complexes in semidilute solutions” (Russia)
15³⁰ – 16⁰⁰	Evgeny Lysenko “Polyelectrolyte complexation of block copolymer micelles with the oppositely charged species: from fundamental aspects to perspective applications” (Russia)
16⁰⁰ – 17³⁰	<i>COFFEE-BREAK and STUDENT POSTERS</i>

Thursday, June 15

<i>Chair: Vladimir G. Sergeev</i>	
11³⁰ – 12⁰⁰	Tatiana Bronich “Change-driven platforms for the delivery of therapeutics” (USA)
12⁰⁰ – 12³⁰	Dominique Hourdet “Structure/properties of macromolecular assemblies based on polyelectrolyte complexes” (France)
12³⁰ – 13⁰⁰	Andrij Pich “Polyampholyte microgels: from tailored synthesis to design of functional materials” (Germany)
13⁰⁰ – 14³⁰	<i>LUNCH</i>

<i>Chair: Dominique Hourdet</i>	
14³⁰ – 15⁰⁰	Elena Chernikova “RAFT polymerization as an instrument for controlled synthesis of amphiphilic copolymers: polymerization induced self-assembly versus conventional solution polymerization” (Russia)
15⁰⁰ – 15³⁰	Oleg Borisov “Effects of topological complexity in macromolecular self-assembly” (Russia/France)
15³⁰ – 16⁰⁰	Igor Erukhimovich “Correlation properties of weakly charged polyelectrolytes under equilibrium association and/or in associating solvent” (Russia)

Friday, June 16

<i>Chair: Renko de Vries</i>	
11³⁰ – 12⁰⁰	Alexey Polotsky “Neutral and charged dendron brushes: structure and properties” (Russia)
12⁰⁰ – 12³⁰	Alexander Yakimansky “Regularly grafted polyimides as a platform for creation of various practically important materials” (Russia)
12³⁰ – 13⁰⁰	Ekaterina Zhulina “Interaction forces between dendronized surfaces” (Russia)
13⁰⁰ – 13¹⁰	<i>CLOSING of the SCHOOL</i>
13¹⁰ – 14³⁰	<i>LUNCH</i>

INVITED LECTURES

USING POLYELECTROLYTE COMPLEXATION IN DE-NOVO PROTEIN DESIGN

Renko de Vries¹

¹ *Physical Chemistry and Soft Matter, Wageningen University, Stippeneng 4, 6708 WE Wageningen, the Netherlands*
renko.devries@wur.nl

Polyelectrolyte complexation is used extensively in biology as a driving force to control both intramolecular and intermolecular association. First I illustrate the broad scope of polyelectrolyte complexation in biology by reviewing of a number of contrasting examples. Next, inspired by the biological examples, I discuss how polyelectrolyte complexation can be used as a driving force for engineering the intramolecular and intermolecular association of de-novo designed proteins. My own work in de-novo protein design is concerned with so-called „protein polymers”, polypeptides with repetitive sequences inspired by natural structural proteins such as collagen, elastin and silk. Examples that I will discuss are: (1) electrostatically driven assembly of virus-like capsids around DNA and RNA (2) electrostatically driven assembly of DNA bottle-brushes (3) control of the activity of antimicrobial peptides.

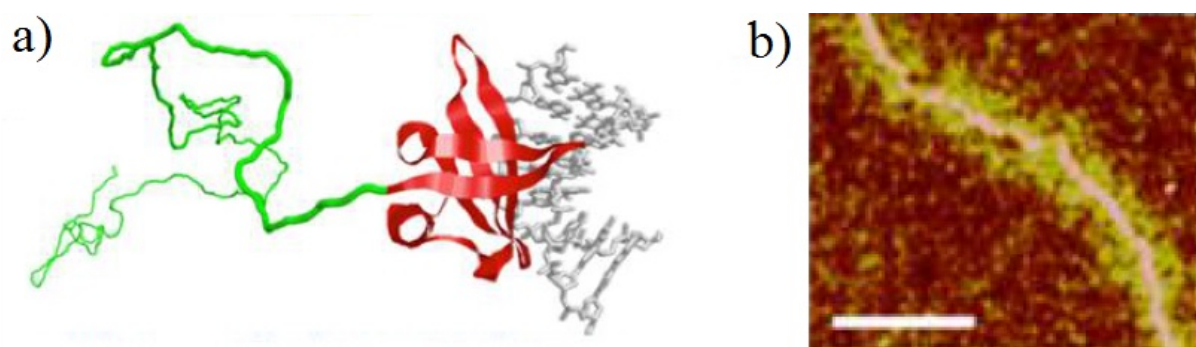


Figure 1. “DNA bottle-brush” assembled from DNA and fusion polypeptide of a DNA-binding domain and a long hydrophilic random chain domain [1].

References

[1] Hernandez-Garcia, A., Estrich, N.A., Werten, M.W.T., van Der Maarel, J.R.C., LaBean, T.H., de Wolf, F.A., Stuart, M/A.C., de Vries, R.: *ACS Nano*, **2017**, accepted for publication, DOI:10.1021/acsnano.6b05938.

BIOINSPIRED MECHANICALLY DURABLE SUPERLIQUIPHILIC/PHOBIC SURFACES

Bharat Bhushan

The Ohio State University, 201 W. 19th Avenue

Columbus, Ohio 43210-1142 USA

bhushan.2@osu.edu <http://www.mecheng.osu.edu/nlbb/>

Living nature, through some 3 billion years of evolution, has developed materials, objects, and processes that function from the nanoscale to the macroscale. The understanding of the functions provided by species and processes found in living nature can guide us to design and produce bioinspired surfaces for various applications¹. There are a large number of flora and fauna with properties of commercial interest. Nature provides many examples of surfaces that repel (hydrophobic) or attract (hydrophilic) water. The most famous is the lotus leaf. Its surface contains a hierarchical structure that, combined with specific surface chemistry, results in a water repellent surface that is self-cleaning, as water droplets collect contaminants as they roll off. Some plant leaves, such as fagus leaves, are hydrophilic, allowing water to rapidly spread into a thin layer, increasing evaporation, leading to a dry and self-cleaning surface. By taking inspiration from nature, it is possible to create hierarchical –structured surfaces with re-entrant geometry and surface chemistry that provide multifunctional properties including superliquiphilicity/phobicity, self-cleaning/low biofouling, and/or low drag. Four different techniques have been developed². A multilayered nanoparticle/binder composite coating has been developed to repel oil and surfactants with self-cleaning properties³. A layer-by-layer technique has been developed that provides surfaces with varying surface chemistry to result in coatings that are hydrophilic/oleophilic, hydrophilic/oleophobic, hydrophobic/oleophilic, or hydrophobic/oleophobic⁴. Nanoparticle-encapsulated⁵ and liquid impregnation⁶ techniques have been developed to create surfaces which repel oil and surfactants. Etched Al surfaces with fluorosilane treatment result in a superoleophobic surface⁷. Some of the nanostructured surfaces have been found to be anti-bacterial⁸. These various techniques provide the basis to fabricate surfaces for a range of applications including self-cleaning, anti-fouling, anti-smudge, anti-fogging, anti-icing, low drag, water purification, and oil–water separation. The coatings have been found to be mechanically durable and some optically transparent.

¹Bhushan, B., *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, Second ed., Springer International, Switzerland, 2016.

²Martin, S., Brown, P. S., and Bhushan, B., “Fabrication Techniques for Bioinspired, Mechanically-durable, Superoleophobic Surfaces for Water, Oil, and Surfactant Repellency,” submitted.

³Martin, S. and Bhushan, B., “Transparent, Wear-resistant, Superhydrophobic and Superoleophobic PDMS Surfaces,” *J. Colloid Interface Sci.* (submitted).

⁴Brown, P. S. and Bhushan, B., “Bioinspired superhydrophilic, superhydrophobic, superoleophilic, superoleophobic coatings prepared by layer-by-layer technique” *Sci. Rep. – Nature* **5**, 14030 (2015).

⁵Brown, P. S. and Bhushan, B., “Durable Superoleophobic Polypropylene Surfaces,” *Phil. Trans. R. Soc. A* **374**, 20160193 (2016).

⁶Brown, P.S. and Bhushan, B., “Liquid-impregnated Porous Polypropylene Surfaces for Liquid Repellency,” *J. Colloid Interface Sci.* (submitted).

⁷Peng, S. and Bhushan, B., “Mechanically Durable Superoleophobic Aluminum Surfaces with Microstep and Nanoreticula Hierarchical Structure for Self-Cleaning and Anti-smudge Properties,” *J. Colloid Surf. Sci.* **461**, 273-284 (2016).

⁸Bixler, G. D. Bhushan, B. et al. “Anti-fouling Properties of Microstructured Surfaces Bio-inspired by Rice Leaves and Butterfly Wings,” *J. Colloid Interf. Sci.* **419**, 114-133 (2014).

COMPLEXES OF ANIONIC LIPOSOMES WITH CATIONIC COLLOIDS: FORMATION, STRUCTURE AND PROPERTIES

Sybachin A.V., Yaroslavov A.A.

Lomonosov Moscow State University, Moscow, 119991, Leninskie Gory, 1-3

E-mail: sybatchin@mail.ru

Spherical lipid bilayer vesicles (liposomes) are widely used for delivery of biological active substances. Hydrophilic compounds can be encapsulated into the inner water cavity of liposomes while the hydrophobic can be embedded into the liposomal membrane. Modification of liposomes with macromolecules can improve physico-chemical properties of vesicles, impart additional properties to liposomal containers or glue several liposomes for creation multi-functional systems.

Small unilamellar liposomes, prepared from mixtures of anionic and zwitterionic lipids, were complexed with polycations – linear polyelectrolytes, polycationic stars and spherical polycationic brushes. To control the complexation and properties of the resulting complexes, the multi-method approach was used including fluorescence spectroscopy, dynamic light scattering, laser microelectrophoresis, cryogenic transmission electron microscopy (cryo-TEM); differential scanning calorimetry, conductometry, etc.

It was demonstrated that the fraction of anionic lipid in liposomes and polycation architecture are the key parameters to the resulted complex structure. Changing of one or both parameters allows one to controllably create either individual polymer-modified liposome or multiliposomal ensemble with desirable composition and colloid stability.

The aggregation stability of liposome/polyelectrolyte complexes, the reversibility of complexation, the integrity of polymer-bound liposomes and to structural rearrangements in the liposomal membrane induced by the polycation chains were shown to depend not only on charge ratio of interacting particles but also on polycation structure. The difference in structures of interfacial complexes formed by macromolecules of different architecture were demonstrated and the complexes were visualised by cryo-TEM. The role of complexation with anionic liposomes on polycations' cytotoxicity was discussed.

Complexation of polycations with liposomes allowed us to obtain structures with cytotoxicity close to toxicity of initial biocompatible liposomal vesicles.

Acknowledgement

This work was supported by Russian Foundation for Basic Research Proj.#17-03-00433

POLYMER-SURFACTANT INTERACTIONS IN SOLUTIONS

Tsarkova L.A.¹, Thiele M.², Davari M.², Schwaneberg U.²

¹ *Moscow State University, Faculty of Chemistry, Moscow, Russia*

² *Lehrstuhl für Biotechnologie, RWTH Aachen University, Aachen, Germany*

E-mail:larisa.tsarkova2@gmail.com

Polymers and surfactants are common ingredients in many products, including paints, inks, cosmetics, adhesives and detergent formulations. There is much that is known about the behavior of each of these ingredients separately, but the dynamic interactions between them in a completed formulation are still the subject of intensive research. It is a fact that the efficacy of polymers can be affected by the presence of surfactants, and vice versa. Within this lecture the types of associations of surfactants with synthetic and biopolymers, such as enzymes, in water-based formulations will be presented, and few of the many suitable methods for measuring the degree of interactions between them will be discussed.

Further, a recent research example will be reported. It concerns a boosted catalytic performance of a protease enzyme assisted by soft nonreactor comprised from like-charged surfactant and polyelectrolytes. The proposed mechanism and novel findings concern established unexpected attractive interactions between negatively charged sulfonated surfactants and macromolecules of fully neutralized polyacrylic acid in the presence of multivalent cations. Performing the experiments using miniaturized wash assay in a wide range of the surfactant concentration disclosed that bridging interaction results in the increased local concentration of the surfactant with the polyelectrolytes chain, resulting in the localized micelle formation at bulk concentrations well below CMC.

Acknowledgement

The experimental work has been supported by HENKEL within the HICAST Program.

POLYELECTROLYTE COMPLEXES IN SEMIDILUTE SOLUTIONS

Ekaterina Litmanovich¹

¹ *Lomonosov Moscow State University, 119991, Moscow, Leninskie Gory, 1
elitmanovich@yandex.ru*

Polyelectrolyte complexes (PEC) - products of the reaction between polyelectrolytes and oppositely charged species: macromolecules, colloidal particles, surfactant micelles. Generally, the reaction of complex formation is studied in dilute solutions, where PEC represent isolated particles of characteristic composition. In this lecture it will be shown that the formation of PEC is a powerful factor in the reversible regulation of the structure and properties of semidilute polyelectrolyte solutions.

Plan of the lecture.

1. Concentration regimes of polymer solutions. Features of the solutions of polyelectrolytes.
2. Experimental methods for determining concentrations of transitions: overlap (C^*) and entanglements formation (C_e). Diagram of concentration regimes of polyelectrolyte solutions.
3. Overlap in solutions of associative polyelectrolytes.
4. Overlap in PEC solutions. The disappearance of semidilute unentangled regime.
5. The difference between the structure of PEC in dilute and semidilute regime.
6. Rheological properties of semidilute PEC solutions.
7. Phase separation in dilute and semidilute solutions of PEC.
8. Features of thermo-sensitive PEC of poly(acrylic acid) and polycations.
9. Rheological properties of semidilute solutions of thermo-sensitive PEC.

POLYELECTROLYTE COMPLEXATION OF BLOCK COPOLYMER MICELLES WITH THE OPPOSITELY CHARGED SPECIES: FROM FUNDAMENTAL ASPECTS TO PERSPECTIVE APPLICATIONS

Lysenko E.A.

Lomonosov Moscow State University, Moscow, Leninskie Gory, 1/3

E-mail: ealysenko@rambler.ru

Spherical polyelectrolyte micelles with the hydrophobic core and lyophilizing charged corona are the products of association of macromolecules of ionogenic amphiphilic block copolymers in aqueous media. Such micelles can be regarded as self-assembling spherical polyelectrolyte brushes, containing huge amount ($\sim 10^3-10^5$) of charged units, concentrated in a star-like fashion around a central core within a small space of several tenths nanometers. Practically all counterions are confined within the micelle corona, producing high osmotic pressure and strong elongation of polyelectrolyte blocks. Due to their unique organization polyelectrolyte micelles possess three characteristic features as counterparts of polyelectrolyte complexation reactions: (a) high binding affinity, (b) high encapsulation capacity and (c) high colloid stabilization capacity for various types of oppositely charged species: polyions, surfactant micelles, proteins, colloid particles, ions of multivalent metals, etc. Polyelectrolyte complexation reactions with participation of block-copolymer micelles as well as structure, properties, and perspective applications of their products - micelle polyelectrolyte complexes (*m-PEC*) - will be the subject of the lecture.

Key aspects that will be discussed are:

- (i) Origins of high affinity of polyelectrolyte micelles towards oppositely charged species, tools for thermodynamic control of polyelectrolyte complexation reactions;
- (ii) Origins of decelerated kinetics of complexation reactions with micelle participation, possibilities of kinetic control over the structure and dispersion stability of *m-PEC* in aqueous media;
- (iii) Structure of *m-PEC* particles;
- (iv) Possibilities of encapsulation of oppositely charged (equally charged in some cases) species within the micelle corona and their effective protection against environmental changes;
- (v) Questions of dispersion stability of *m-PEC* particles with block copolymer micelles acting as a host or a guest polyelectrolyte;
- (vi) Perspectives of *m-PEC* application as nanocontainers, effective drug delivery vehicles, surface modification agents and nanoreactors.

On the whole we will see that *m-PEC* indeed may constitute a novel class of polyelectrolyte complexes with a promising potential of further fundamental and technological development.

CHANGE-DRIVEN PLATFORMS FOR THE DELIVERY OF THERAPEUTICS

Bronich T.

*Department of Pharmaceutical Sciences and Center for Drug Delivery and Nanomedicine,
University of Nebraska Medical Center,
985830 Nebraska Medical Center, Omaha, NE 68198-5830, USA
E-mail: tbronich@unmc.edu*

Self-assembled block copolymer micelles are widely utilized in pharmaceuticals for development of novel therapeutic and diagnostic modalities. Recently nanofabrication of polymer micelles was significantly advanced by exploring charge driven self-assembly of block copolymers containing ionic and nonionic blocks (“block ionomers”). These block copolymers react electrostatically with oppositely charged species such as polyions, proteins, surfactants, or metal ions and form block ionomer complexes (BIC). These complexes self-assemble into particles of nanoscale size and form stable aqueous dispersions. The latter enable, uniquely, encapsulation of charged therapeutic molecules. The block ionomer-metal complexes can be used as templates to synthesize a novel type of entirely hydrophilic polymer micelles with cross-linked ionic cores. These core-shell materials represent nanosized gels with the core comprising a swollen network of crosslinked polyions surrounded by a nonionic polymer shell. The stimuli-responsive behavior of nanogels can be easily controlled by selection of constituent polymer and crosslinker components to achieve a desired response at the site of action, which imparts nanogels the ability to participate actively in the intended function of the carrier system rather than being passive carriers of their cargo. Chemical functionalization of nanogels with various ligands was also explored for targeted drug delivery, triggered drug release, or preparation of composite materials. Hybrid nanogels containing hydrophobic domains in the hydrophilic cross-linked cores were designed to provide for combinatorial therapy resulting in simultaneous delivery of several anticancer drugs with very different physical properties and mechanisms of action. Further studies on the design, synthesis, and animal testing of nanogels as carriers for multidrug delivery will be described.

STRUCTURE/PROPERTIES OF MACROMOLECULAR ASSEMBLIES BASED ON POLYELECTROLYTE COMPLEXES

Dominique Hourdet^{1,2}

¹*Laboratoire Sciences et Ingénierie de la Matière Molle, CNRS, ESPCI Paris,
PSL Research University, 10 rue Vauquelin, F-75005 Paris, France.*

²*Laboratoire Sciences et Ingénierie de la Matière Molle, Université Pierre et Marie Curie,
Sorbonne-Universités, 10 rue Vauquelin, F-75005 Paris, France.*

dominique.hourdet@espci.fr

Associating polymers have received considerable attention over the past thirty years due to their very high potential in a wide range of fields such as enhanced oil recovery, cosmetics, paints or biomedical applications like drug release or tissue engineering. Nowadays, the interest is still very strong with the design of macromolecular architectures of increasing complexity based in particular on the development of supramolecular chemistry. When dealing with attractive interactions in aqueous media, different mechanisms come to mind such as hydrophobic interactions or the formation of electrostatic complexes; each of which bringing their own specificity and responsiveness [1]. In this presentation, we will show how hydrophobic and electrostatic interactions can be coupled within macromolecular architectures in order to reversibly control their self-assembly in aqueous media [2-3]. Such behavior is illustrated in **Figure 1**, where the introduction of ionisable groups, either anionic (**A**) or cationic (**C**), into thermoresponsive poly(N-isopropylacrylamide) chains (**PNIPA**) provides a versatile platform to tune the phase separation process and the rheological properties using temperature, pH, and/or ionic strength as environmental triggers [3].

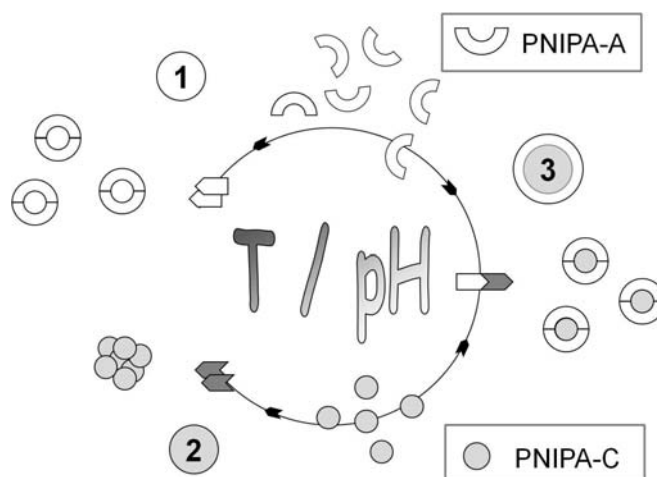


Figure 1. Responsive macromolecular assemblies in aqueous solutions.

References

- [1] Philippova, O. E., Hourdet, D., Audebert, R., Khokhlov, A. R.: *Macromolecules*, **1996**, 29, 2822
- [2] Bokias, G., Vasilevskaya, V. V., Iliopoulos, I., Hourdet, D., Khokhlov, A. R.: *Macromolecules*, **2000**, 33, 9757
- [3] Siband, E., Tran, Y., Hourdet, D.: *Macromolecules*, **2011**, 44, 8185

POLYAMPHOLYTE MICROGELS: FROM TAILORED SYNTHESIS TO DESIGN OF FUNCTIONAL MATERIALS

Andrij Pich, Wenjing Xu, Ricarda Schröder

DWI Leibniz Institute for Interactive Materials eV., RWTH Aachen University, Aachen, Germany, Forckenbeckstr. 50
pich@dwilrwtth-aachen.de

Aqueous polymer microgels bearing ionisable groups are interesting macromolecular colloidal structures with a strong application potential in drug delivery, biomaterials, adsorbents and coatings. In a large family of polyelectrolyte microgels polyampholyte microgels exhibit extraordinary properties due to the co-existence of oppositely charged groups in crosslinked polymer networks. Such colloids can invert their surface charge or exhibit reversible ionic crosslinks at different pH leading to the strong change in the size and swelling degree.

Present paper will present an overview about synthesis, characterization, functionalization and application of polyampholyte microgels as building blocks for design of functional materials. In particular, different synthesis methods (precipitation polymerization, polymerization in W/O emulsion) will be described that allow application of different molecular reactive building blocks (monomers, macromonomers, crosslinkers) and control the amount and distribution of ionisable groups and charges in microgels. Using controlled synthesis methods microgels with controlled size, narrow size distribution and statistical, [1] core-shell [2,3] and Janus-like distribution of ionisable groups were synthesized.

The behavior of polyampholyte microgels in aqueous solutions was investigated to understand their properties like swelling/deswelling, charge modulation and colloidal stability. The experimental data combined with theoretical calculations and simulations indicate that amount, distribution and balance between ionisable groups in microgels govern their properties in aqueous solutions.

Ampholyte microgels were used as cargo for the uptake/release of polyelectrolytes and proteins, colloidal templates for the biomineralisation as well as building blocks for design of functional biointerface coatings. [4-5]

Acknowledgement

Authors thank DFG SFB 985 “Microgels and Microgel Systems” and VW Stiftung for financial support of this work.

References

- [1] Schroeder, R.; Rudov, A. A.; Lyon, L. A.; Richtering, W.; Pich, A.; Potemkin, I. I. *Macromolecules* **2015**, *48*, 5914-5927.
- [2] S. Schachschal, A. Balaceanu, C. Melian, D. Demco, T. Eckert, W. Richtering, A. Pich, *Macromolecules* **2010**, *43*, 4331- 4339.
- [3] W. Richtering, A. Pich, *Soft Matter* **2012**, *8*(45), 11423-11430.
- [4] A. S. Sechi, S. Ullmann, J. M. G. Freitas, R. P. Takehara, P. Wünnemann, R. Schröder, M. Zenke, A. Böker, G. Aydin, S. Rütten, Andrij Pich, *Adv Mater Interf*, **2016**, DOI [10.1002/admi.201600455](https://doi.org/10.1002/admi.201600455).
- [5] M. Kather, M. Skischus, P. Kandt, A. Pich, G. Conrads, S. Neuss, *Angew Chem Int Ed*, **2016**, DOI: [10.1002/anie.201609180R1](https://doi.org/10.1002/anie.201609180R1).

RAFT POLYMERIZATION AS AN INSTRUMENT FOR CONTROLLED SYNTHESIS OF AMPHIPHILIC COPOLYMERS: POLYMERIZATION INDUCED SELF-ASSEMBLY VERSUS CONVENTIONAL SOLUTION POLYMERIZATION

Chernikova E.V.

*Lomonosov Moscow State University, Faculty of Chemistry, Polymer Department,
Moscow, 119991, Leninskie Gory, 1, bld.3
E-mail: chernikova_elen@mail.ru*

The growing progress in the development of the processes of reversible deactivation radical polymerization (RDRP) led to creation of new smart polymers with well-defined chain architectures. Among them, amphiphilic copolymers, and in particular block copolymers, causes particular interest due to ability to spontaneous self-assembly with formation of different nanostructures. The type of nanostructure and the capability to respond to external physical or chemical stimuli depends on chemical structure of the chain, monomer unit distribution and chain length. All these parameters may be tuned in the course of RDRP. Among RDPR techniques, the RAFT processes have certain advantages, including resistance to the functional groups of monomers and a broad range of solvents and temperature intervals. These advantages provide the possibility to direct synthesis of amphiphilic copolymers both in organic and aqueous media.

The solution technique of controlled synthesis of amphiphilic block copolymers requires the choice of appropriate solvent, RAFT agent and the sequence of the monomer addition in the polymerization. The change in thermodynamic quality of the solvent during polymerization in this case may cause violation of the living mechanism. The typical examples of such kind of the synthesis using polyacrylic acid and its copolymers bearing trithiocarbonate group will be discussed [1–3].

The second approach basing on various types of heterophase polymerization (dispersion, emulsion, and miniemulsion) may lead to self-assembly of the amphiphilic block copolymers directly in the course of RAFT polymerization [4]. As a result, the dispersions of “core–shell” particles of different morphology are formed. The stability of the synthesized dispersions, control over particles morphology and molecular mass characteristics of the resulted block copolymers governed by the range of parameters will be discussed in details [1–3].

The advantages and disadvantages of both techniques will be considered.

Acknowledgement

This work was financially supported by the Russian Science Foundation (project № 15-13-30007).

References

- [1] Chernikova E. V., Plutalova A. V., Mineeva K. O., Nasimova I. R., Kozhunova E. Yu., Bol'shakova A. V., Tolkachev A. V., Serkhacheva N. S., Zaitsev S. D., Prokopov N. I., Zezin A. B. *Polymer Science, Ser. B*, **2015**, 57 (6). 547-559.
- [2] Chernikova E.V., Plutalova A.V., Mineeva K.O., Vishnevetski D.V., Lysenko E.A., Serkhacheva N.S., Prokopov N.I. *Polymer Science, Ser. B*, **2016**, 58 (5), 564-573.
- [3] Chernikova E.V., Serkhacheva N.S., Smirnov O.I., Prokopov N.I., Plutalova A.V., Lysenko E.A., Kozhunova E.Yu. *Polymer Science, Ser. B*, **2016**, 58 (6), 629-639.
- [4] Charleux B., Delaittre G., Rieger J., D'Agosto F. *Macromolecules*, **2012**, 45, 6753-6765.

EFFECTS OF TOPOLOGICAL COMPLEXITY IN MACROMOLECULAR SELF-ASSEMBLY

Borisov O.V.^{1,2,3}, Zhulina E.B.^{1,2}

¹ *Institute of Macromolecular Compounds of the Russian Academy of Sciences,
199004, St.Petersburg, Bolshoy pr. 31*

² *St.Petersburg National University of Information Technologies, Mechanics and Optics,
197101 St.Petersburg, Kronverkskii pr. 49*

³ *Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les
Matériaux, F-64053, 2 av. P.Angot, Pau, France
E-mail: oleg.borisov@univ-pau.fr*

Self-assembled polymer nanoparticles find numerous applications in soft nanotechnology and in medicine. For these applications a control over dimensions and morphology of the nanoparticles is highly important. We discuss theoretical principles of design of the smart multicompartment polymer nanoparticles by solution assembly of block copolymers with varied architecture. The statistical thermodynamic approach is applied to predict how the morphologies of the polymer nanoparticles can be controlled by combination of intramolecular solvophilic/solvophobic balance and macromolecular topology. In particular, we consider self-assembly of microarm stars and linear-dendritic block copolymers with either soluble or insoluble dendron blocks. We demonstrate how by changing the topology and degree of branching of one of the blocks different nanostructures (spherical or cylindrical wormlike micelles or polymersomes) can be assembled. Multicompartment polymer nanoparticles can be obtained by assembly of triblock terpolymers and we demonstrate how the theoretical model enables us to predict the shape and number of various compartments as a function of the terpolymer composition and architecture.

CORRELATION PROPERTIES OF WEAKLY CHARGED POLYELECTROLYTES UNDER EQUILIBRIUM ASSOCIATION AND/OR IN ASSOCIATING SOLVENT

Erukhimovich I.Ya.

*A.N.Nesmeyanov Institute of Organoelement Compounds of RAS Russia,
119991, GSP-1, Moscow, V-334, Vavilova St. 28, INEOS
ierukhs@polly.phys.msu.ru*

The main result of the fluctuation theory of weakly charged polyelectrolytes developed by the author and Borue [1] (see also Refs [2-5]) was prediction of the order-disorder transitions (microphase separation) of such polyelectrolytes in a solvent, which would be poor for the referent neutral polymer. Therewith, the polymer-solvent interaction has been supposed to be well described in terms of the Flory-Huggins χ -parameter.

The idea to describe the aqueous polyelectrolyte solutions and the very notions of hydrophobicity and hydrophilicity in terms of χ -parameters seems now to be a sort of common knowledge. Meanwhile, it is not so obvious that the properties of polymers (polyelectrolytes) in systems with and without an equilibrium hydrogen bonds' network do not differ essentially due to the corresponding structural effects. To enlighten the issue, a theory of a model equilibrium (annealed) network of labile bonds developed earlier [6,7] has been extended to describe the correlations of fluctuations in such systems [8]. I present some new results that picture clearly the distinctions between the fluctuation effects of associating and non-associating polyelectrolytes in associating and non-associating solvents. In particular, the results by Kramarenko et al [9,10] concerning the effect of the ion pairs and multiplets formation on the spinodal stability of the salt polyelectrolytes' solutions are generalized/

References

- [1] Borue, V. Yu.; Erukhimovich, I. Ya. *Macromolecules* 1988, 21, 3240.
- [2] Joanny, J.-F.; Leibler, L. *J. Phys.* 1990, 51, 545.
- [3] Nyrkova, I. A.; Khokhlov, A. R.; Kramarenko Ye.Yu. *Polymer science USSR*, 1990, 32, 852. [4] Dobrynin, A. V.; Erukhimovich, I. Ya. *Sov. Phys. JETP* 1991, 72, 751.
- [5] Dormidontova, E. E.; Erukhimovich, I. Ya.; Khokhlov, A. R. *Macromol. Theory Simul.* 1994, 3, 661.
- [6] Erukhimovich, I. Ya. *JETP* 1995, 81, 553.
- [7] Erukhimovich, I.Ya.; Tamm, M. V.; Ermoshkin, A. V. *Macromolecules* 2001, 34, 5653.
- [8] Erukhimovich, I. Ya. *Polym. Sci* 2016 (to be published).
- [9] E.Yu. Kramarenko, I.Ya. Erukhimovich and A.R. Khokhlov, *Macromol. Theory & Simul.* 2002, **11** (5), 462-471.
- [10] E.Yu. Kramarenko, I.Ya. Erukhimovich and A.R. Khokhlov, *Polymer Science, ser. A* 2004, 46 (9), 974-984.

NEUTRAL AND CHARGED DENDRON BRUSHES: STRUCTURE AND PROPERTIES

Polotsky A.A.^{1,2}, Prokacheva V.M.³, Kazakov A.D.³, Birshstein T.M.^{1,3},

¹ *Institute of Macromolecular Compounds, Russian Academy of Sciences, 199004, Bolshoy pr. 31, St. Petersburg, Russia*

² *Saint Petersburg National Research University of Information Technologies, Mechanics, and Optics (ITMO University), Kronverkskiy pr. 49, 197101 St. Petersburg, Russia*

³ *Physics Department, Saint Petersburg State University, Ulyanovskaya ul. 1, 198504 Petrodvorets, St. Petersburg, Russia*
alexey.polotsky@gmail.com

Polymer brushes - monolayers of polymer chains densely grafted onto impenetrable substrates - belong to the most popular and intensively studied polymer systems. In the last few years there exists a huge interest to a new class of polymer brushes, where not the traditional linear chains but macromolecules of branched topologies, in particular, regularly branched dendrons, are grafted onto a substrate. Theoretical and simulation approaches typically used to study dendron brushes include Monte Carlo and molecular dynamic simulation, self-consistent field numerical methods, and various analytical approaches.

Theoretical studies revealed that dendron and star brushes (the star brush is equivalent to the first generation dendron brush) have specific properties that are associated with their non-trivial internal structure. At high grafting densities, dendrons' packing in a planar brush results in a relatively uniform and smooth density profile. Because of the branched architecture of grafted macromolecules, this can be achieved by separation of dendrons into two or more groups, or populations, differing in the degree of stretching. This remarkable feature of dendron brushes will be discussed in detail. Effect of the charge on the structure of dendron brushes will be discussed, both cases of polyelectrolyte dendron brushes with fixed charge and pH-sensitive dendron brushes will be considered.

The peculiarities of the internal structure of dendron brushes allows using them as matrices for "molecular switches". To demonstrate this, the behavior of a single linear chain embedded into a star brush will be considered. It will be shown that the chain may undergo sharp conformational coil-to-flower transition triggered by a change in the brush grafting density or in the solvent quality (equivalent to temperature variation). Thus, it is possible to control the linear chain conformation by changing the properties of the matrix. In the case of dendron polyelectrolyte brushes, the number of ways to control the brush properties increases (one can vary the ionic strength or the degree of ionization), and in the final part of the talk the behaviour of a non-charged chain in a polyelectrolyte star brush will be discussed.

Acknowledgements

This work is supported by a Marie Curie International Research Staff Exchange Scheme Fellowship (PIRSSES-GA-2013-612562 - POLION) within the seventh European Community Framework, by the Russian Science Foundation (grant 16-13-10485), and by the Government of Russian Federation (grant 074-U01).

REGULARLY GRAFTED POLYIMIDES AS A PLATFORM FOR CREATION OF VARIOUS PRACTICALLY IMPORTANT MATERIALS

Yakimansky A.V., Meleshko T.K., Ivanov A.V., Ivanova A.S., Kashina A.V., Tyan N.S., Polotskaya G.A.

*Institute of Macromolecular Compounds, Russian Academy of Sciences,
Bolshoi pr. 31, 199004 St. Petersburg, Russia
yakimansky@yahoo.com*

Regularly grafted copolyimides (polyimide brushes) PI-g-PMMA, PI-g-PMAA, and PI-g-PDMAEMA (Fig. 1) with polyimide (PI) backbones and polymethylmethacrylate (PMMA), polymethacrylic acid (PMAA), and poly(N,N-dimethylamino-2-ethylmethacrylate) (PDMAEMA) are synthesized by ATRP method.

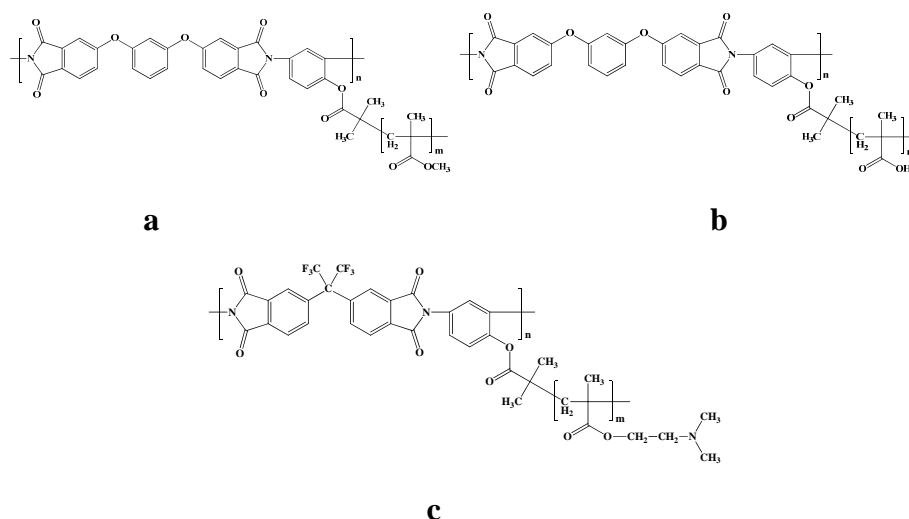


Fig. 1. Structure of polyimide brushes (a) PI-g-PMMA, (b) PI-g-PMAA, and (c) PI-g-PDMAEMA.

It is shown that efficient pervaporation membranes for dehydration of alcohols with the pervaporation separation index $PSI > 70000$ may be prepared from PI-g-PMMA. Moreover, film membranes cast from blends of PI-g-PMMA polyimide brushes with commercially available matrix polymers, like poly(m-phenylene-iso-phthalamide), showed high productivity and selectivity upon pervaporation separation of methanol-hexane mixtures, obviously, due to microphase separation providing favorable conditions for diffusion of permeate molecules through channels formed by interfaces.

It was demonstrated by experiments *in vitro* and *in vivo* that PI-g-PMAA brushes are promising for biomedical applications as nanocontainers for efficient and selective delivery of cyanoporphyrine agents of photodynamic theranostics to tumor cells.

Polyimide brushes PI-g-PDMAEMA proved to be efficient nanoreactors for the synthesis of stable aqueous dispersions of silver nanoparticles with the mean size of ~ 10 nm and narrow size distribution which could be used in biomedicine and optoelectronics.

The work is supported by the Russian Science Foundation (grate no. 14-13-00200).

INTERACTION FORCES BETWEEN DENDRONIZED SURFACES

Zhulina E.B.^{1,2}, Leermakers F.A.M.³ Borisov O.V.^{1,2,4}

¹ *Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russ*

² *St. Petersburg National University of Informational Technologies, Mechanics and Optics, 197101 St. Petersburg, Russia*

³ *Physical Chemistry and Soft Matter, Wageningen University, 6703 NB Wageningen, The Netherlands*

⁴ *Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR 5254, CNRS, UPPA, Pau, France*

kzhulina@hotmail.com

Dendronized interfaces have recently attracted a lot of attention as a novel class of polymer-modified surfaces. When regularly branched macromolecules are end-tethered to a solid substrate at high grafting density, inter-dendron contacts dominate over intra-molecular ones and a brush of dendrons exhibits novel features compared to a brush of linear macromolecules. A significant part of experimental and theoretical research in the field of polymer brushes now focuses on exploring "topological" dimension in the design parameter space. This direction of research is motivated by a promise to create thinner protective layers to ensure steric repulsion between polymer-decorated particles and, at the same time, offer many terminal segments that can be used for functionalizations.

We present a comprehensive update on the research of brushes formed by branched macromolecules with the emphasis on the effect of chain architecture on the steric repulsion and lubrication properties. Theoretical insights into the structural properties of the dendron-modified surfaces are obtained with the analytical SS-SCF self-consistent field theory based on the strong-stretching (SS) approximation. The analytical predictions are systematically compared to the results of the numerical Scheutjens-Fleer self-consistent field (SF-SCF) modeling. The theory allows for a unified description of the impact of branching on the stabilizing properties of dendron brushes [1]. We discuss also a cyclized architecture of the tethered polymer [2], and present the results showing that apposing brushes of macrocycles exhibit a relatively low interpenetration length. This is in line with MD simulations [3] which showed a low friction coefficient in the linear regime of lubrication for brushes composed of tethered macrocycles compared to linear chain brushes under similar conditions.

We therefore argue that there is an important role of chain architecture to control colloidal stability and lubrication properties of surfaces with polymer brushes.

References

[1] Borisov O.V., Zhulina E.B., Polotsky A.A., Leermakers, F.A.M., Birshtein, T.M.

Macromolecules **2014**, *47*, 6932

[2] Zhulina E.B., Leermakers, F.A.M., Borisov, O.V. *Macromolecules* **2016**, *49*, 8758

[3] Erbas, A.; Paturej, J. *Soft Matter* **2015**, *11*, 3139

POSTER SESSION

COLLOID-CHEMICAL PROPERTIES OF ANIONIC AQUEOUS DISPERSIONS OF IONOMER POLYURETHANES BASED ON POLYESTERS

Golovanova K.V., Shilova S.V., Galyametdinov Y.G., Zenitova L.A.

Kazan national research technological university,

Kazan, K. Marx St., 68

E-mail: k.v.golovanova@gmail.com

The interest in the development of formulations of aqueous polyurethane dispersions (depending on the choice of raw materials find their application as adhesives, coatings and impregnating compositions) is due not only to care for the environment (lower emissions of organic solvents) [1], but also the possibility of production of low-viscosity polymers with high molecular weight (due to the solubilization of hydrophobic ionomer dispersed phase in an aqueous medium).

The objects of study of colloidal-chemical properties of the synthesized dispersions based on polyesters (PEA, PEBA, PBA), the aromatic diisocyanate is 2,4-toluylendiisocyanate (TDI), macrochain extension – 1,6-hexandiol (HD), ionogenic agent – 2,2-bis-(hydroxymethyl) propionic acid (HDPA) and dimethylethanolamine as carboxyl groups neutralizer (DMEA).

Composition and colloidal-physical properties of the obtained dispersions are presented in table 1

Table 1. The results of the measurements

Composition	Contents of the hard blocks, %	Dry matter, %	Viscosity, mPa×s	pH	particle Size, nm	Interfacial angle Glass*/MDF**/PVC film ***
PEBA +TDI+HD+HDPA+DMEA	23,8	50±3%	390	7,35	75-110	65,4 / 87,2 / 36
PEA +TDI+HD+HDPA+DMEA	23,5	50±3%	293,7	7,42	54-91	63,6 / 75,9 / 54,9
PBA+TDI+HD+HDPA+DMEA	24,6	50±3%	265	7,5	32-65	38,5 / 79,2 / 51,3

* GOST ISO 9385-2013; ** GOST P53208-2008; *** GOST 24944-81

Kinetic characteristics of aqueous dispersions of anionic ionomer polyurethanes depend on the surface properties of the contacting phases and the pH of the environment. A shift of pH values in the acidic region and the increase of particle sizes >500 nm, and reduces the stability of the anion-active dispersions [2]. Data in the table 1 characterize the obtained aqueous polyurethane dispersions as sustainable. Currently compositions lifetime is more than 6 months.

Links:

[1] Meyer-Vastus Ulrich, Polyurethanes. Coatings, adhesives, sealants. - M.: Paint-Media 2009,. – 400S. [2] Levchenko N. I., Sukhorukov S. A., Travinskaya T. V. // partnerships polymers. Churchill College, University. Cambridge. 1996. P. 195-200.

PORPHYRIN-POLYMER INTERACTIONS - A KEY TO CONTROL THE CHROMOPHORE AGGREGATION STATE IN AQUEOUS MEDIA

Gradova M.A.¹, Zhdanova K.A.², Bragina N.A.², Lobanov A.V.¹

¹ *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Kosygin Str., 4*

² *Moscow Technological University, Moscow, Vernadsky Pr., 86*

E-mail: m.a.gradova@gmail.com

Porphyrin derivatives are considered as promising photosensitizers due to the high extinction coefficients and fluorescence quantum yields. However, their photophysical properties are strongly dependent on the aggregation state of the chromophores, which tend to self-associate in polar solvents due to either hydrophobic or amphiphilic nature of their macrocycles. Therefore, it is necessary to develop an easy way to control the aggregation behavior of the porphyrin-based photosensitizers in aqueous media and to prevent molecular self-association. The aim of this work is to establish the relationships between the molecular structure of the polymer and its possible ways of intermolecular interaction with the porphyrin derivatives. The report compares the aggregation behavior of different porphyrins in polyvinylpyrrolidone (PVP), potassium poly(vinyl sulfate) (PVS) and sodium poly(styrene sulphonate) (PSS) solutions at various *pH* values. The porphyrins studied included four tetraphenylporphyrin derivatives with either electron-donating (–OH, –OCH₃) or electron-withdrawing (–COOH, –COOCH₃) groups in *para*-positions of the phenyl rings. All these porphyrins readily undergo protonation in acidic medium (*pH* < 3) resulting in the formation of positively charged dicationic species.

Besides the electrostatic interactions, the results suggest a crucial role of π – π stacking between the polymer phenyl rings and the porphyrin aromatic systems in the monomer form stabilization of the chromophore, which is in consistence with the previous findings [1-3]. This is probably due to the predominance of the porphyrin-polymer π – π interactions leading to the fluorescent monomer stabilization over the porphyrin-porphyrin stacking resulting in the non-specific aggregate formation and the total fluorescence quenching. For this reason anionic PSS containing aromatic groups demonstrates the selective binding of diprotonated monomer species of all the porphyrins studied in acidic medium. It was also found that hydrogen bonding is very important in the ladder-type *J*-aggregate self-assembly of the porphyrin building blocks. From the data obtained the apparent binding constants and stoichiometry of the resulting porphyrin-polymer supramolecular complexes were calculated. Thus, a diversity of intermolecular interactions in the porphyrin-polymer systems allows to control the aggregation state of the chromophores in aqueous solutions, and hence, provides an easy way to design porphyrin-based *pH*-controlled smart materials.

The work was financially supported by RFBR (Project 15-03-03591).

Literature

- [1] Toncelli C., et al. *Dyes and Pigments*, **2013**, 98, 51-63.
- [2] Gomez-Tardajos M., et al. *Dyes and Pigments*, **2013**, 99, 759-770.
- [3] Pino-Pinto J.P., et al. *Dyes and Pigments*, **2017**, 139, 193-200.

STRUCTURE AND PROPERTIES OF ORGANIC ZEOLITE LIKE MEMBRANES BASED ON WEDGE-SHAPED AMPHIPILES

Grafskaia Kseniia N.^{1,2}, Anokhin Denis V.^{1,2}, Zhu Xiaomin³ and Ivanov Dimitri A.^{1,2,4}

¹Lomonosov Moscow State University, Faculty of Fundamental Physical and Chemical Engineering, Moscow, 119991, GSP-1, 1-51 Leninskie Gory, Russia.

²Moscow Institute of Physics and Technology (State University), Dolgoprudny, 141700, Institutskiy per. 9, Russia

³DWI – Leibniz-Institute for Intractive Materials e.V. and Institute for Technical and Macromolecular Chemistry of RWTH Aachen University, D-52056 Aachen, Forkenbeckstr. 50, Germany

⁴Institut de Science de Matériaux de Mulhouse (IS2M-CNRS), F-68057 Mulhouse, 15 rue Jean Starcky, France

E-mail: grafskayaxeniya@gmail.com

We report on new approach for fabrication of zeolite-like bicontinuous cubic structure from pyridinium salt of wedge-shaped mesogens. The thermodynamically metastable cubic phase is formed after thermal treatment of thin film in saturated methanol vapors. The substitution of pyridinium counter-ion by sodium one prevents formation of cubic phase. The found structure is stable in temperature range from 25 to 100 °C because of local ordering of linear alkyl side groups. Stability of dry cubic phase allows to replace methanol in 3D channels by water during swelling in humid atmosphere. The resulting swollen cubic phase shows formation of water channels with radius of 28 Å and water uptake up to 16. The structural models of the material in dry, partially swollen and fully swollen states were proposed. Below room temperature the cubic phase transforms to thermodynamically stable lamellar phase because of ultimate swelling in precipitated water. The proposed mechanism of non-covalent stabilization of metastable bicontinuous phase can help in development of new functional materials built via self-assembly process.

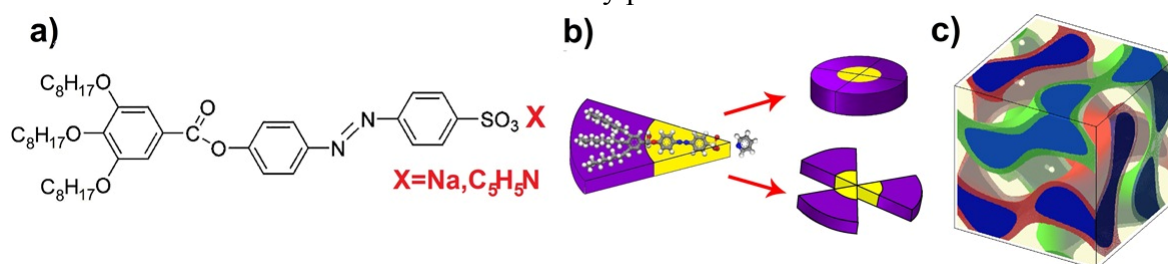


Figure 1. Chemical structure of mesogen (a). Amphiphilic self-assembly (b). Schematic structure of cubic gyroid phase (c).

Acknowledgements

The research was supported by the Russian Science Foundation (project №16-13-10369).

References

[1] K. Grafskaia, B. Zimka, X. Zhu, D. Anokhin, D. Ivanov, *AIP Conf.Proc.*, **2016**, 1748, 040009.

THE CONFORMATION AND COMPOSITION OF COMPLEX AND SULFONATED IONOMERS SURFACTANT MOLECULES IN A META-XYLENE

I.A. Karavaev¹, M.Y. Kudryashov¹

¹*Moscow Technological University, 119454, Moscow, Prospekt Vernadskogo street, 86
e-mail: mister.karavaev@inbox.ru*

Solutions of the polymer – surfactant were investigated by methods of viscosity, transitional diffusion, high-speed sedimentation and refractometry. The used polymer was sulfonated polystyrene (SPNa) (1.35 , 2.5 and 5.8 mol % SO₃Na groups, which are distributed statistically) Z=1000, Mw/Mn = 1.05. The used surfactant was AOT (aerosol OT). The used solvent was m-xylene. At ratio of 30 molecules of surfactant on 1 SO₃Na group in solution was detected the existence of complexes of polymer – surfactant and micelles of surfactants. Molecular weight and composition of the detected complexes were estimated by molecular hydrodynamics and refractometry methods. The weakening of sorption properties of polymer with dilution of solution was established for complexes SPNa 2.6 and 5.8. This could be described by the competing effect on the free energy of the system between the increase in transport mobility of surfactant micelles upon dilution and changes in intermolecular shielding molecules surfactants of ionic groups in ionomer.

COMPLEXES BETWEEN POLYCATIONS AND MULTICOMPONENT ANIONIC LIPOSOMES

Kostenko S.N., Efimova A.A.

*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3,
119991, Moscow, Russia*

E-mail: stepankostenko@mail.ru

Liposomes are widely used in medicine and biology as a convenient model for studying the structure and properties of biological (cell) membranes and for the encapsulation of biologically active compounds. Modification of liposomal containers by polymers increases the circulation lifetime and affinity to the target cells. The ability of liposomes to simulate the biomembrane behavior is useful for the analysis of cell interaction with synthetic water-soluble polymers, in particular, polyelectrolytes. In most studies, liposomes are formed from a mixture of two or several lipids. Meanwhile, the membranes of plants, animals and microorganisms contain (in addition to lipids) amphiphilic compounds of another nature, for example, cholesterol (Chol). When using liposomes as nanocontainers for drug delivery antioxidant is commonly embedded into the bilayer for preventing lipid oxidation. However, the influence of cholesterol and / or antioxidant incorporated in the lipid membrane on the properties of the liposome-polycation complexes remains practically unexplored.

In this study the interaction of linear polycations (poly-N-ethyl-4-vinylpyridinium bromide, polylysine, chitosan) with multicomponent anionic liposomes formed of electroneutral and negatively charged lipids and containing cholesterol-and/or antioxidant ionol was investigated. We analyzed the composition and stability of complexes at water-salt media, the integrity of the membrane in contact with polycations and the changes in properties of complexes with time. The results of this investigation are of interest for preparing liposomal containers for drug encapsulation and for predicting the behavior of polyelectrolytes on the surface of cells and the reaction of the cellular membranes to the adsorbed polymer.

Acknowledgement

This work was supported by Russian Science Foundation (project 14-13-00255).

INTERACTION OF ANIONIC LIPOSOMES WITH SYNTHETIC LINEAR POLYCATIONS

Lentin I.I., Kostenko S.N., Efimova A.A.

*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3,
119991, Moscow, Russia
E-mail: weerit@yandex.ru*

For last decades bilayer lipid vesicles (liposomes) have been used as nanocontainers for encapsulation and delivery of biologically active substances. Modification of liposomes by means of polyelectrolytes increases the circulation lifetime, the affinity to the cell membranes and could affect the efficiency of drug delivery. The ability of liposomes to simulate the cell membrane behavior is intensively used for the investigation of polyelectrolyte-cell interaction, in particular, for polyelectrolytes that are used for stimulating immune response and DNA transfection.

In this work we investigated the interaction of synthetic linear polycations (polylysine and caustamine) with anionic liposomes formed of electroneutral phosphatidylcholine and negatively charged diphosphatidylglycerol (cardiolipin) by means of laser microelectrophoresis, dynamic light scattering, conductometry and fluorescence spectroscopy. Polylysine and caustamine could adsorb on the surface of negatively charged liposomes. The interaction is accompanied by surface charge neutralization, aggregation of the particles and quenching of the fluorescence of label, embedded into the lipid bilayer. Interaction of liposomes with polylysine is reversible: polycation is removed from the liposomal surface by NaCl addition. The contact of liposomes with caustamine is irreversible. Adsorption of polylysine and caustamine is accompanied by defect formation in the bilayer. In the case of polylysine we found out leakage of 30% of salt from the inner liposomal volume in 24 h after polymer adsorption. For caustamine this value is equal to 100%. The thickness of the polylysine adsorption layer is approx. 25 nm, for caustamine it was found to be less than 3 nm. Thus, the properties of the studied polyelectrolyte- liposome complexes strongly depends on the polycation nature and on the thickness of the polymer layer on the surface of the lipid membrane.

Acknowledgement

This work was supported by Russian Science Foundation (project 14-13-00255).

NANOCONTAINERS BASED ON CHITOSAN AND ANIONIC LIPOSOMES

Mulashkin F.D.¹, Efimova A.A.¹, Krivtsov G.G.², Melik-Nubarov N.S.¹, Evtushenko E.G.¹, Rudenskaya G.N.¹, Yaroslavov A.A.¹

¹ *Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3, 119991, Moscow, Russia*

² *Mechnikov Research Institute of Vaccines and Sera, Maly Kazenny pereulok, 5a, 105064, Moscow, Russian Federation*

E-mail: fedor.mulashkin@gmail.com

The application of liposomes as nanocontainers for drug delivery was suggested decades ago. Multi-liposome assembly composed of liposomes loaded with different fillings could enable controlled delivery of the medicines in a desirable ratio. This method allows to magnify the therapeutic action of drugs and to propose a simple and reliable technology for producing multi-functional drugs for a particular patient.

In this work we suggest a universal approach for preparation of biodegradable multiliposomal containers through electrostatic adsorption of anionic liposomes on the surface of cationic chitosan nanoparticles without additional modification of both components. Chitosan is a commercially available polycationic biopolymer of natural origin that is generally obtained by alkaline deacetylation from chitin, which is the main component of the exoskeleton of crustaceans. Chitosan is known for being biocompatible and biodegradable. The integrity of liposomes in liposome-chitosan conjugates is retained. Each chitosan particle could adsorb up to one hundred anionic liposomes, that allows to magnify the therapeutic action of drugs. The conjugates demonstrate stability towards dissociation in physiological media. The complexes are biodegradable: eventually decompose after being attacked by hydrolytic enzymes which makes them promising for use in the field of drug delivery. It is found that chitosan-liposome complex and the products of its biodegradation are non-toxic in a wide range of concentrations. Thus, the findings of this work seem to be promising for creation of biodegradable multiliposomal complexes as containers for encapsulation and release of biologically active substances.

Acknowledgement

This work was supported by Russian Science Foundation (project 14-13-00255).

CHITOSAN BASED SELF-ASSEMBLED NANOPARTICLES FOR PASSIVE DELIVERY OF ANTITUMOR DRUGS

Raik S.V.^{1,2}, Kritchenkov A.S.¹, Poshina D.N.¹, Skorik Y.A.¹

¹ *Institute of Macromolecular Compounds of the Russian Academy of Sciences, St. Petersburg, Bolshoy pr. V.O., 31*

² *Saint Petersburg State Chemical Pharmaceutical Academy, St. Petersburg, ul. Prof. Popova, 14A*
E-mail: raiksv@gmail.com

Nowadays, cancer is one of the main causes of human death. Existing anticancer chemotherapy have many undesired side effects because of the high toxicity of anticancer drugs. One possible way to overcome this drawback is to use nano-delivery systems. Current evidence confirms that nanoparticles of about 10–400 nm tend to accumulate in tumors due to the increased blood circulation and reduced lymphatic drainage of tumor tissues. Thus, a significant accumulation of antitumor drugs in tumor tissues (the so-called enhanced permeability and retention effect) could be expected with the correct choice of polymer for fabrication of these nano-carriers. Chitosan, a polycation, has important advantages for use as a nano-platform for targeted delivery, including its biodegradability, biocompatibility, and low cost. Chitosan is also a nonallergenic and nontoxic biopolymer.

In our previous work, we proposed a nano-delivery system for taxanes (paclitaxel and docetaxel) using an ionic gelation technique of water-soluble polyampholyte succinyl-chitosan (SC) with sodium tripolyphosphate [1]. In this study, we investigated two strategies of nanoparticles design: (i) modification of SC [2] with cholesterol for the preparation of micelle-like drug loaded nanoparticles, and (ii) direct conjugation of hydrophobic anticancer drug paclitaxel with SC *via* succinate linker. Conjugation of succinyl-cholesterol and succinyl-paclitaxel with SC was performed using carbodiimide method. Polymers were dialyzed against distilled water, lyophilized, and then redispersed in water and sonicated.

Dynamic light scattering measurements showed the decrease of hydrodynamic diameter and ζ -potential of self-assembled nanoparticles with a degree of hydrophobic functionalization (DF_{Chol} and DF_{PT} for cholesterol and paclitaxel, respectively). Optimal DF_{Chol} was found to be in the range of 5-10%; further increase of cholesterol content led to undesired aggregation of nanoparticles. When $DF_{\text{Chol}} < 5\%$, we observed the formation of relatively large nanoparticles with a hydrodynamic diameter higher than 300 nm and ζ -potential higher than -20 mV that might have worse tumor accumulation. Conjugation of paclitaxel with ($DF_{\text{PT}}=3\%$) led to the formation of nanoparticles with narrow size distribution and hydrodynamic diameter of 280 nm and ζ -potential of -13 mV.

Aknowledgements

This work was financially supported by the Russian Foundation for Basic Research (no.15-04-06664).

References

- [1] Skorik Y.A., Golyshev A.A., Kritchenkov A.S., Gasilova E.R., Poshina D.N., Sivaram A.J., Jayakumar R. *Carbohydrate Polymers*, 2017, 162: 49–55.
[2] Golyshev A.A., Moskalenko Y.E., Skorik Y.A. *Russian Chemical Bulletin*, 2015, 64: 1168-1171.

FLUORINATED TETRAPHENYLPORPHYRINS IMMOBILIZED ON SULFOCATIONIC POLYMERS AS THE CATALYSTS OF PHOTOOXIDATION PROCESSES

Shershnev I.V.¹, Kopylov A.S.¹, Glagolev N.N.¹, Bragina N.A.², Solovieva A.B.¹

¹ *Institute of Chemical Physics RAS, 119991, Moscow, Kosygina str. 4*

² *Moscow Technological University, 119454, Moscow, Prospekt Vernadskogo 78*

E-mail: shershnev.ilya@gmail.com

Photocatalytic systems based on fluorinated tetraphenylporphyrins (FTFP) immobilized on sulfocationic copolymer MF-4SK were for the first time prepared in nonpolar environment of supercritical carbon dioxide (SC-CO₂). The impact of immobilization conditions (temperature and pressure of SC-CO₂, reaction time, presence of co-solvent) and a polymer carrier structure on the content of porphyrins in the polymer were studied. It was shown that the rate constant of anthracene photooxidation in SC-CO₂ medium in the presence of prepared systems extremely depended on the content of the porphyrin and the thickness of the polymer carrier used in the form of films. The catalytic activity of heterogeneous porphyrin photosensitizers is comparable to the efficiency of soluble porphyrin catalysts in the oxidation of organic and in aqueous media. But heterogeneous porphyrin photosensitizers significantly more stable than soluble porphyrin under irradiation and can be used up to 7 - 8 times in photooxidation reactions practically without loss of activity. The increased stability of immobilized FTFP ensured the absence of solvation of the reactants in a SC-CO₂ and the formation of strong intermolecular bonds between porphyrins and macromolecules MF-4SK. This allows reuse of immobilized FTFP in photooxidation reactions in an aqueous medium substantially without loss of activity.

Acknowledgements

This work was supported by Russian Science Foundation (RSF) - project 16-13-10295 (efficacy study of obtained systems in singlet oxygen photogeneration in various media) and the Russian Foundation for Basic Research (RFBR) - project 16-32-00557 (study of porphyrins immobilization in polymeric carriers in SC-CO₂ environment).

INTERPLAY BETWEEN THE RHEOLOGICAL PROPERTIES AND STRUCTURE OF NATURAL POLYSACCHARIDE (XANTHAN) NETWORKS

Shibaev A.V.¹, Mityuk D.Yu.^{1,2}, Muravlev D.A.^{1,2}, Philippova O.E.¹

¹ Faculty of Physics, Moscow State University, 119991 Moscow, Leninskie Gory, 1, bld. 2

² Gubkin Russian State University of Oil and Gas, 119991 Moscow, Leninskiy av., 65

E-mail: shibaev@polly.phys.msu.ru

Natural polyelectrolytes can form hydrogels with high mechanical properties even at low polymer concentrations (less than 0.1%), therefore they are widely used as thickeners in food, oil industry etc. In this work, we investigate the mechanical properties and structure of natural rigid polysaccharide (xanthan) gels in the presence of a low molecular weight salt, with or without cross-linker – chromium chloride.

The structure of xanthan networks was visualized by FF-TEM, and microphase separation was observed, with polymer-rich areas (network skeleton) containing aggregated xanthan double helices. The skeleton thickness grows upon the increase of polymer concentration or the addition of cross-linker, which means the increase of tendency to microphase separation. This results in higher elastic modulus in the presence of cross-linker, but its weaker dependence on polymer concentration for cross-linked networks than for non-cross-linked ones. This is due to the fact that skeleton thickness in the absence of cross-linker is small, and the main contribution to the elasticity of the gel upon deformation is made by compression or stretching of the skeleton fragments. In the presence of cross-linker, the skeleton is thicker, and only a bending deformation of its parts is possible. It is also shown that xanthan macromolecules within the network have sharp kinks due to the presence of short flexible segments probably being single xanthan helices, which join rigid double helix segments.

Thus, it was shown that xanthan gels without or with cross-linker are microphase-separated, and their rheological properties strongly depend on the microstructure of the polymer network and, in particular, on the thickness of the polymer skeleton.

Acknowledgement

This work was supported by the Russian Science Foundation (project № 15-13-00114).

References

- [1] Philippova O.E., Shibaev A.V., Muravlev D.A., Mityuk D.Yu., *Macromolecules*, **2016**, *49*, 6031
- [2] Shibaev A.V., Abrashitova K.A., Kuklin A.I., Orekhov A.S., Vasiliev A.L., Iliopoulos I., Philippova O.E., *Macromolecules*, **2017**, *50*, 339

ROLE OF CATIONIC GROUP STRUCTURE IN BIOLOGICAL ANTIMICROBIAL ACTIVITY OF AMMONIUM POLYELECTROLYTES

Yulia Simonova

*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow
119991, Russia, Leninsky prosp. 29
simonova@ips.ac.ru*

In polyelectrolyte (PE) rows, polyamines with primary, secondary and tertiary ammonium groups in links are of the especial interest. A range of monomers for obtaining of such PE is narrow. Among those monomers, diallylamine (DAA) in the nonquaternary form and its derivatives are promissory. An approach has been developed that is essentially based on the creation in the polymerizing medium of a dominant amount of DAA monomers in protonated form, as a result of which the competitive ability of the side chain transfer reaction diminishes and chain transfer allyl radical transforms into the propagation radical [1,2]. The secondary/tertiary diallylammonium polymers (PDAAs) may be defined as the representatives of a novel family of synthetic polyelectrolytes which properties are differ from those of quaternized analogues. In particular, this is confirmed by PDAAs, unlike quaternary polymers of this series, featuring biological antimicrobial efficacy of broad spectrum including rare activity against mycobacterium *M. tuberculosis* [3].

In recently investigations on equivalent conductivity of dilute aqueous solutions of diallylammonium PE with different amine structure in links and various counteranions, the strong correlation has been shown between these PE dissociation and ionization degree and their activity against mycobacterium *M. tuberculosis* [4]. The results [3,4] have revealed a crucial role of the polyelectrolyte nature of these polymers in mechanism of their antimicrobial activity. At the same time, hydrogen bonding between secondary/tertiary PDAAs and molecules of outer bilayer can play a noticeable role in the disturbance of structure and integrity of the characteristic mycobacterial outer membrane, which has been evidenced to have a small negative charge [3].

Acknowledgement

Author is grateful to Dr. Larisa Timofeeva for her valuable help in the discussion of results.

References

- [1] Timofeeva L., Vasilieva Y., Kleshcheva N., Gromova G., Topchiev D.: *Int. J. Quantum. Chem.*, **2002**, 88, 531.
- [2] Timofeeva L., Kleshcheva N., Vasilieva Y., Gromova G., Timofeeva G., Filatova M.: *Polym Sci Ser A* **2005**, 47, 273.
- [3] Timofeeva, L., Kleshcheva, N., Shleeva, M., Filatova, M., Simonova, Yu., Ermakov, Yu., Kaprelyants, A.: *Appl. Microbiol. Biotechnol.*, **2015**, 99, 2557.
- [4] Timofeeva, L.M., Balakaeva I.V., Lileev A.S., Simonova Yu.A., Lyaschenko A.K. *Polym. Sci. Ser. C*, **2017** (in print).

AFM, KELVIN PROBE FORCE MICROSCOPY AND DLS STUDY OF BIOGENIC SELENIUM-CONTAINING NANOSYSTEMS BASED ON POLYELECTROLYTE COMPLEXES

T.E. Sukhanova¹, M.P. Temiryazeva², S.V. Valueva¹, M.E. Vylegzhanina¹, A.Ya. Volkov¹,
A.A. Kutin¹, A.G. Temiryazev²

¹*Institute of Macromolecular Compounds RAS, 199004 St.-Petersburg, Russia,*

²*Kotelnikov Institute of Radio Engineering and Electronics (Fryazino Branch) RAS,
141190 Fryazino, Moscow oblast, Russia*

tat_sukhanova@mail.ru

The research reported here is focused on the developing of new hybrid nanosystems based on polyelectrolyte complexes and Se⁰ nanoparticles. To accomplish this goal, we used polyelectrolyte complexes (PECs) of sodium dodecyl sulfate (SDS) with the cation copolymer (CC) P(VP-C) of *N*-vinylpyrrolidone (VP) and *N,N,N*-triethyl-*N*-methacryloyloxyethylammonium iodide (C) for Se⁰ nanoparticles stabilization. The Se⁰ nanoparticles are formed in aqueous solutions of PECs with different composition using redox reaction between selenious and ascorbic acids as we previously reported in [1-3]. These complexes show different bioactivities depending on the molar ratio of charged subunits γ ($\gamma = \text{SDS/C}$) in the complex [3]. Since these PECs have membranotropic properties and drastically increase the permeability of lipid bilayers, we assumed that they increase the selenium activity. The main goal of this paper was to evaluate the morphology, structure and electrical characteristics novel Se⁰/PEC nanosystems by atomic force (AFM), Kelvin probe force microscopy (KPFM) and dynamic light scattering (DLS) methods. The unique morphology and the inhomogeneity of the surface potential distribution in thin films of Se⁰/PEC nanosystem were confirmed by KPFM method for the first time in our previous work [4]. It has been found, that at the “special point” $\nu = 0.1$, filled and hollow nano- and microcapsules and micelles formed in the system.

To examine the synthesized nanosystems with different γ values while varying the Se⁰/PEC mass ratio (ν), at first, self-organization of Se⁰/PEC nanosystems and starting components in aqueous solutions was studied by UV-vis spectrophotometry. Then, the average hydrodynamic radii of nanostructures were determined by DLS. Using AFM and KPFM methods, we showed that nanostructures significantly differed in their morphological organizations can be formed via varying synthesis conditions. Developing hybrid nanosystems proposed as carriers for targeting drug delivery in medical applications.

1.Sukhanova T.E., Valueva S.V., Vylegzhanina M.E., Kutin A.A., Derylo-Marczewska A. Ch. 6 in “Selenium: Dietary Sources, Properties and Role in Human Health”, Ed. W. Morrison, Nova Science Publishers, Inc., New York, USA, 2015, pp. 123-146.

2.Sukhanova T.E., Valueva S.V., Vylegzhanina M.E., et al. // J. Surf. Invest.: X-Ray, Synchrotron and Neutron Tech. 2014. V.8. No.3. pp. 484-493.

3.Valueva S.V., Sukhanova T.E., Sokolova M.P., et al. // Rus. J. Phys. Chem. A, 2015, Vol. 89, No. 1, pp. 92–98.

4.Sukhanova T.E., Temiryazeva M.P., Vylegzhanina M.E., et al. // State-of-the-art trends of scientific research of artificial and natural nanoobjects, STRANN 2016. AIP Conf. Proc. 2016. Vol. 1748. P. 020003-1–020003-7.

REMOTE INTERACTION OF RARE CROSSLINKED POLYMER STRUCTURES OF POLYACRYLIC ACID AND AMBERSEP 920 U DURING NEODYMIUM IONS SORPTION

Jumadilov T.K., Kondaurov R.G., Khakimzhanov S.A.

JSC "Institute of chemical sciences after A.B. Bekturov", Almaty, Kazakhstan

E-mail: sergali1994@inbox.ru

It is known, that ion exchange resins and polymer hydrogels are related to high-selective polymer structures, which contain functional groups acting as ligands in complex formation with metal ions, what can occur by ionic or donor-acceptor mechanism. This facilitates such polymers possessing sorption capabilities towards metal ions including ions of rare earth elements. The sorption of Nd^{3+} ions by intergel system has been studied: weakly acid hydrogel of polyacrylic acid (hPAA) containing functional acid carboxyl groups $-\text{COOH}$ and industrial ion exchange resin Ambersep 920 U. In addition, the remote interaction and mutual activation of polymers have been studied.

The distance interrelationship of hPAA and Ambersep 920 U polymers in water environment (distillated water) has been studied. It is evident from the swelling coefficient results of the individual polymers in intergel system, that in case of hPAA this factor increased from 12 for system where only hPAA exists, and then, during decrease of its correlation passes through maximum value $C_{\text{sw}} = 24$ in equal correlation of polymers. Swelling coefficient value of ion-exchange resin Ambersep 920 U rapidly increases from 2 (normal for ion exchange resins) and reaches maximum value of 6.8 (normal for hydrogels) after 6 hours of presence in water environment. So, these values imply that mutual activation of polymers in intergel system due to formation of highly ionized structure of polymers.

From sorption results it has been established that, in relation to ion Nd^{3+} in water solvent with concentration $C(\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}) = 30 \text{ mg/l}$ the highest sorption activity was demonstrated by intergel system in molar ratio of polymers hPAA : Ambersep 920 U, as 4 : 2 after 1 day from start of sorption with extraction degree of 45%, and also individual polymer hPAA after 3 hours after start of sorption with extraction degree of 66,7%. At the same time, electroconductivity of neodymium nitrate solution lowers by decreasing neodymium ions concentration as a result of sorption process. Also, by analyzing solutions' pH data it was determined that solutions' acidity increased during sorption process due to substitution of H^+ ions with Nd^{3+} ions in polymer structure thus expelling latter into the solution. Comparing the polymers' swelling coefficients in distillated water and in neodymium nitrate solution, it has been determined that swelling coefficient in the mention salt solution become lower as sorption goes on due to polymer links becoming less ionized and polymer molecules striving to more energetically efficient form – globe.

POLYSACCHARIDE-BASED CRYOSTRUCTURATES AS MATERIALS FOR BIOMEDICAL APPLICATIONS

N. D. Zvukova¹, R. V. Ivanov¹, A. V. Tsiskarashvili², and V. I. Lozinsky¹

¹ A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow; e-mail: natalya_zvukova@mail.ru

² Central Research Institute of Traumatology and Orthopedics named after N. N. Priorov, Ministry of Health of the Russian Federation, ul. Priorova 10, Moscow

Polymeric cryostrucurates are macroporous spongy materials prepared by freezing polymer–solvent systems followed by sublimation (or cryoextraction) of the crystalline phase of the frozen solvent and subsequent transformation of the resultant macroporous polymeric material to the insoluble state. Cryostrucurates based on such nontoxic, biocompatible polymers, as proteins and polysaccharides, are promising as dressings for healing of wounds and burns and as matrices for drug storage and controlled release.

In this study, macroporous alginate- and chitosan-based cryostrucurates have been synthesized by moderate freezing (–10 to –30°C) of 1–5 wt % aqueous solutions of sodium alginate and chitosan acetate, respectively, followed by solvent sublimation and treatment of the resulting sponges with ethanolic solutions of CaCl₂ (or H₂SO₄) and NH₃, respectively (Fig. 1).

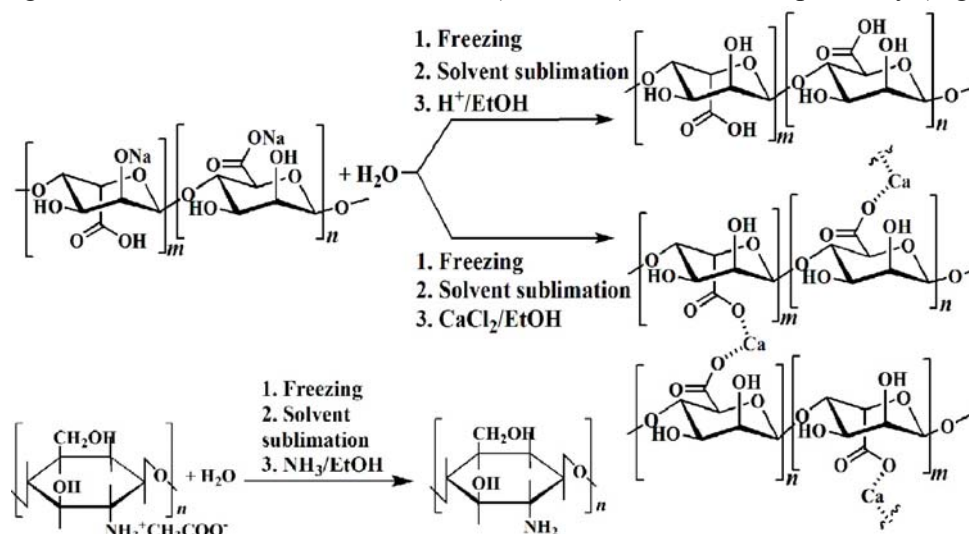
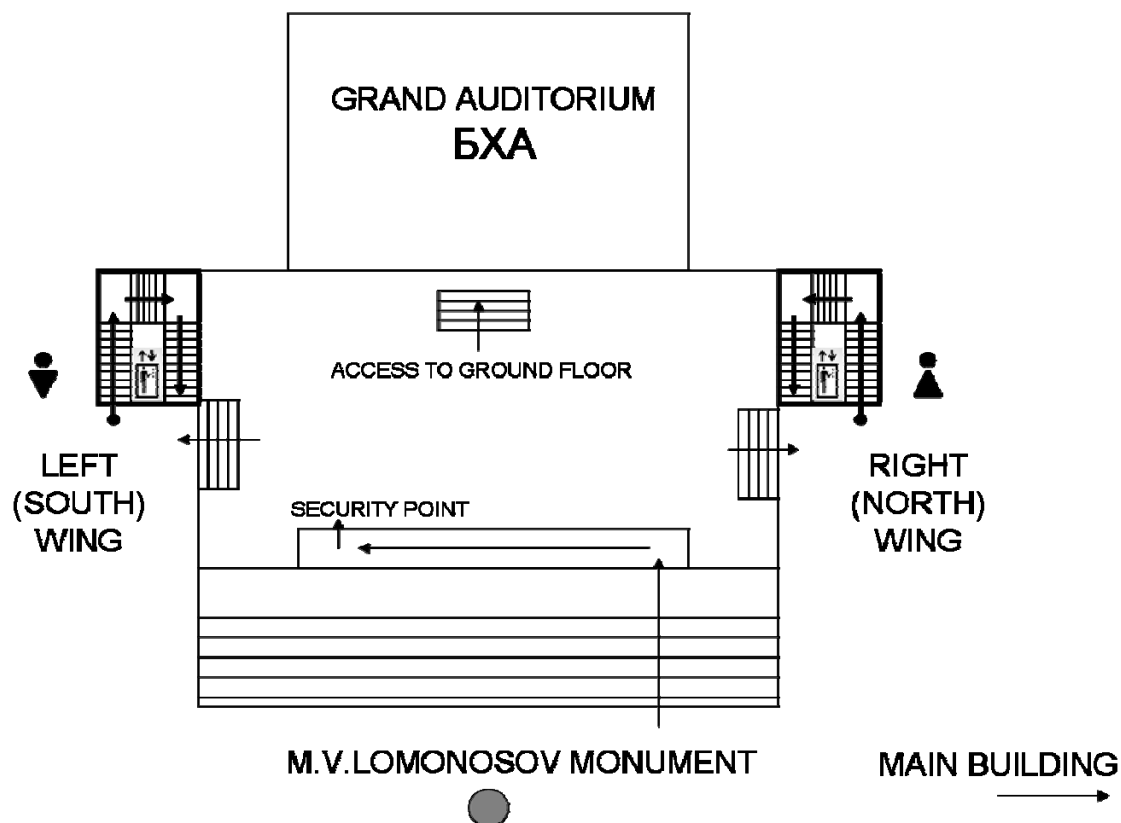


Fig. 1. The Scheme of the alginate and chitosan based cryostrucurates syntheses

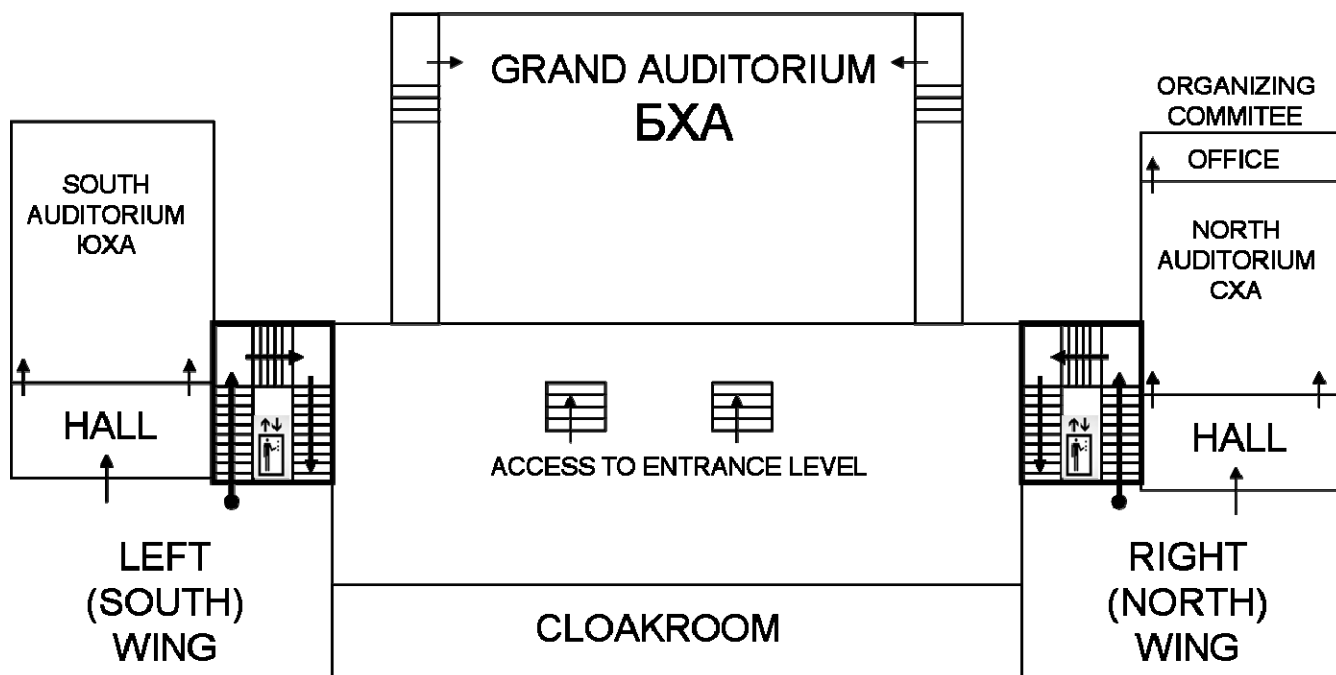
It has been shown that the degree of swelling of the sponges depends on the polysaccharide concentration in initial solutions and does not, virtually, depend on the freezing temperature. The morphology of the cryostrucurates has been studied by optical microscopy. The sponges thus obtained have been successfully tested as polymer matrices for controlled release of nanocolloidal silver and several antibiotics.

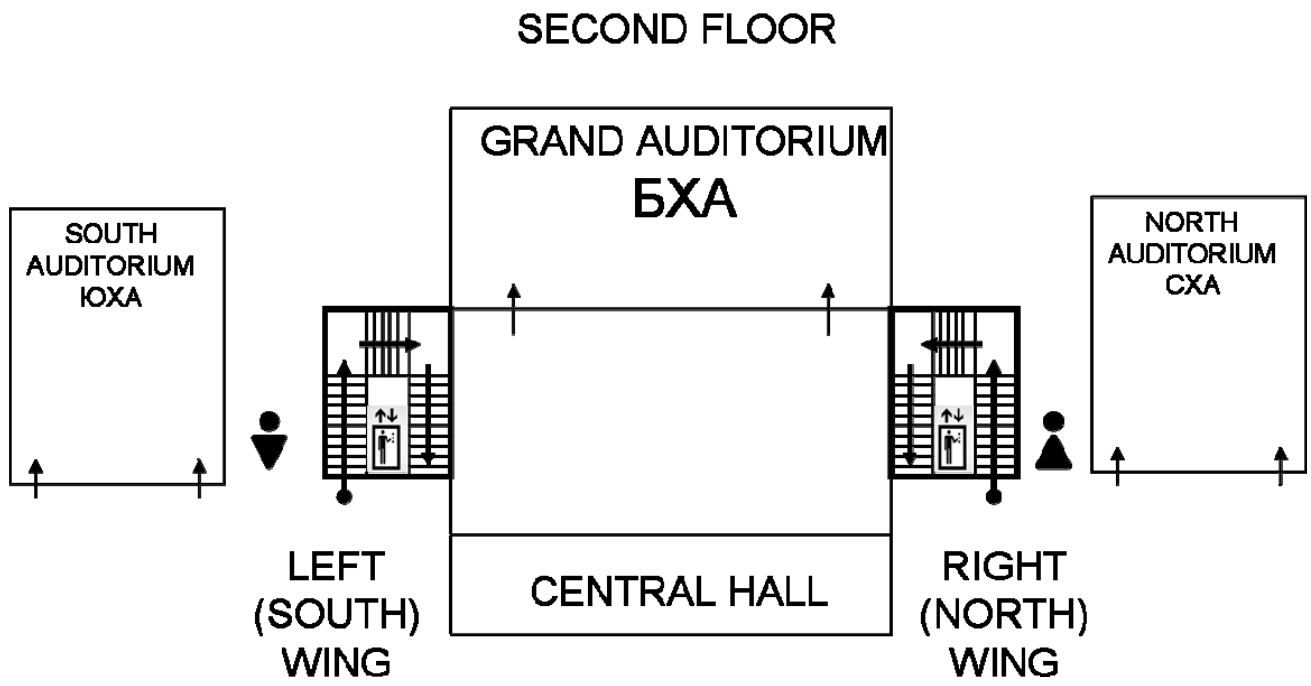
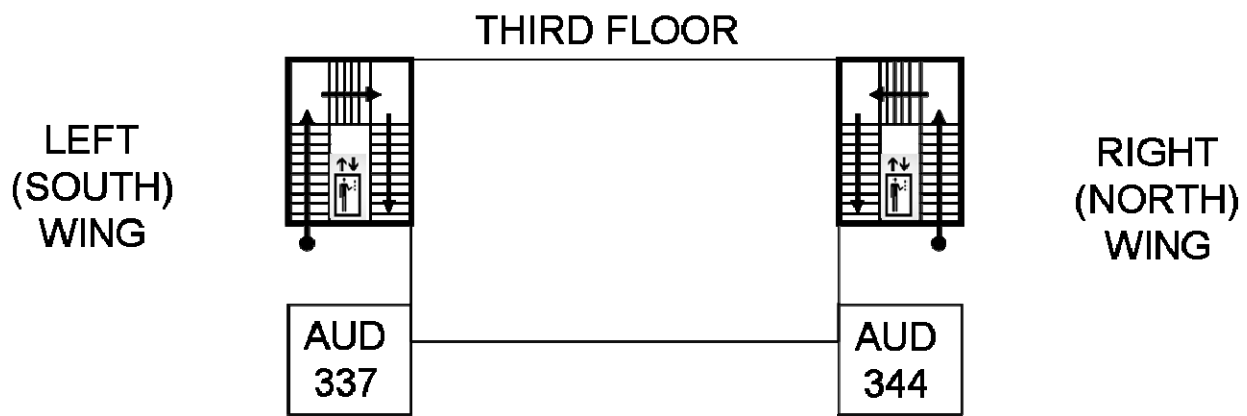
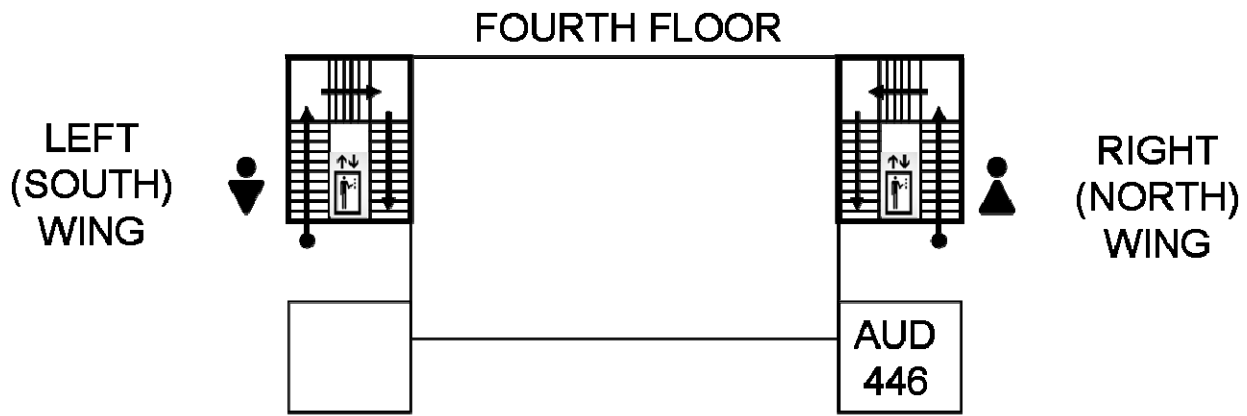
The work was supported by Russian Science Foundation; project no. 16-13-10-365

**CHEMISTRY DEPARTMENT BUILDING SCHEME
FIRST FLOOR (ENTRANCE LEVEL)**

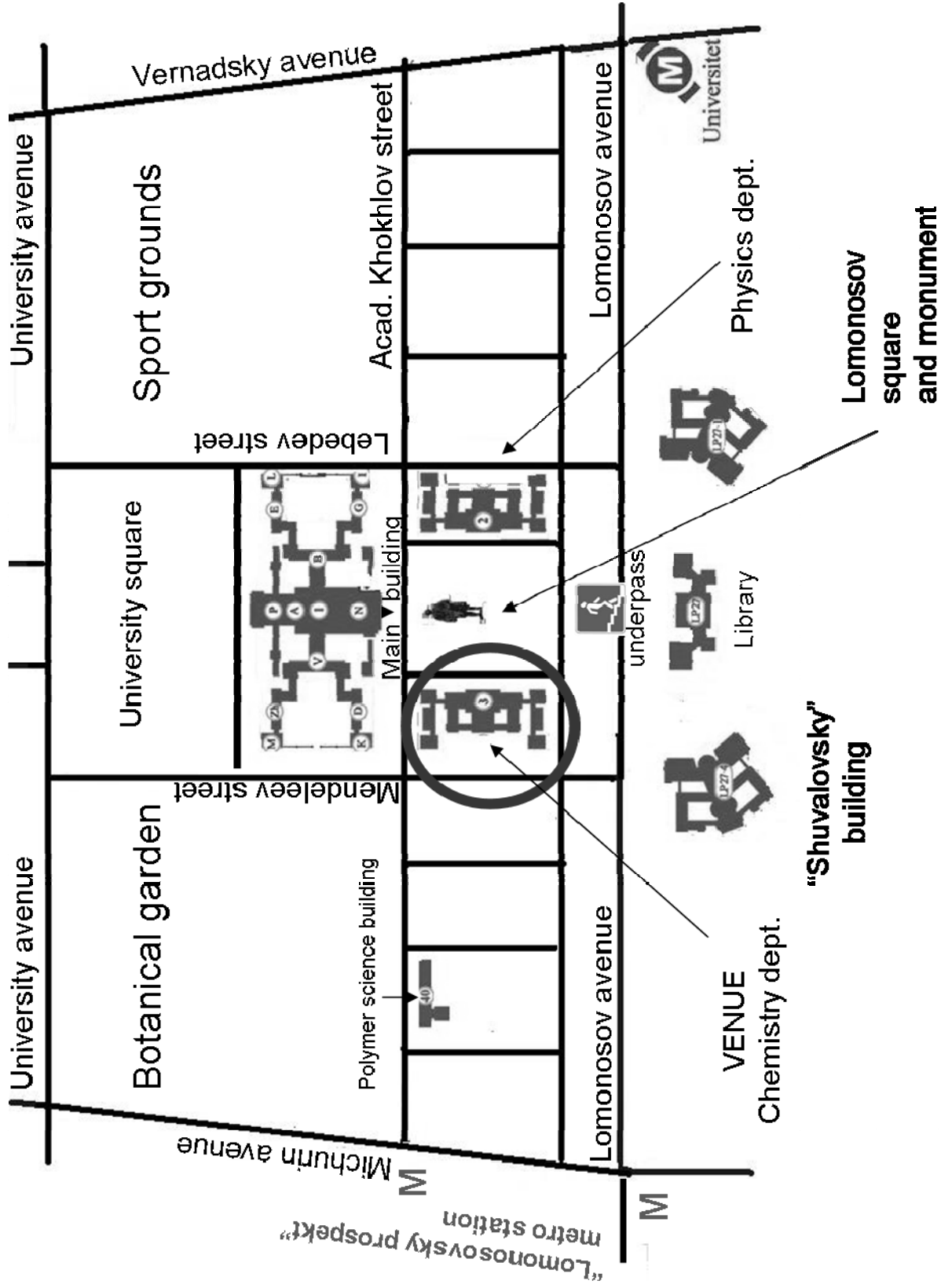


GROUND FLOOR ("-1")





↑
access to Moscow sightseeing point



University avenue

Botanical garden

University square

Sport grounds

Michurn avenue
M
"Lomonosovsky prospekt"
metro station

Mendeleev street

Lebedev street

Polymer science building

Main building

Acad. Khokhlov street

Vernadsky avenue

Lomonosov avenue

Lomonosov avenue



"Shuvalovsky"
building



Library



underpass



Physics dept.



Universitet

VENUE
Chemistry dept.

Lomonosov
square
and monument