INSTITUTE OF MACROMOLECULAR
CHEMISTRY AS CR

INTERNATIONAL UNION OF PURE
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10 - 14 JULY 2016 PRAGUE

SELF-ASSEMBLY IN THE WORLD OF POLYMERS

80th

PRAGUE MEETING
ON MACROMOLECULES

BOOK OF ABSTRACTS AND PROGRAMME

INSTITUTE OF MACROMOLECULAR CHEMISTRY
ACADEMY OF SCIENCES OF THE CZECH REPUBLIC

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

SELF-ASSEMBLY IN THE WORLD OF POLYMERS

10 – 14 July 2016, Prague

80th PRAGUE MEETING ON
macroMOLECULES

Book of Abstracts and Programme

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TABLE OF CONTENTS

80th PRAGUE MEETING ON MACROMOLECULES

under the auspices of the
International Union of Pure and Applied Chemistry

Organized by the Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic

Petr Štěpánek
Conference Chairman

Jiří Kotek
Director of the Institute

Daniela Illnerová, Marie Rodová, Dana Horká
Local Organizing Team

Josef Jůza, Jiří Kaprálek
Technical Support

Address:
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
Heyrovského nám. 2
162 06 Prague 6
Czech Republic

Phone: (+420) 296 809 331
Fax: (+420) 296 809 410
E-mail: sympo@imc.cas.cz
Website: http://www.imc.cas.cz

Conference Chairman

Petr Štěpánek

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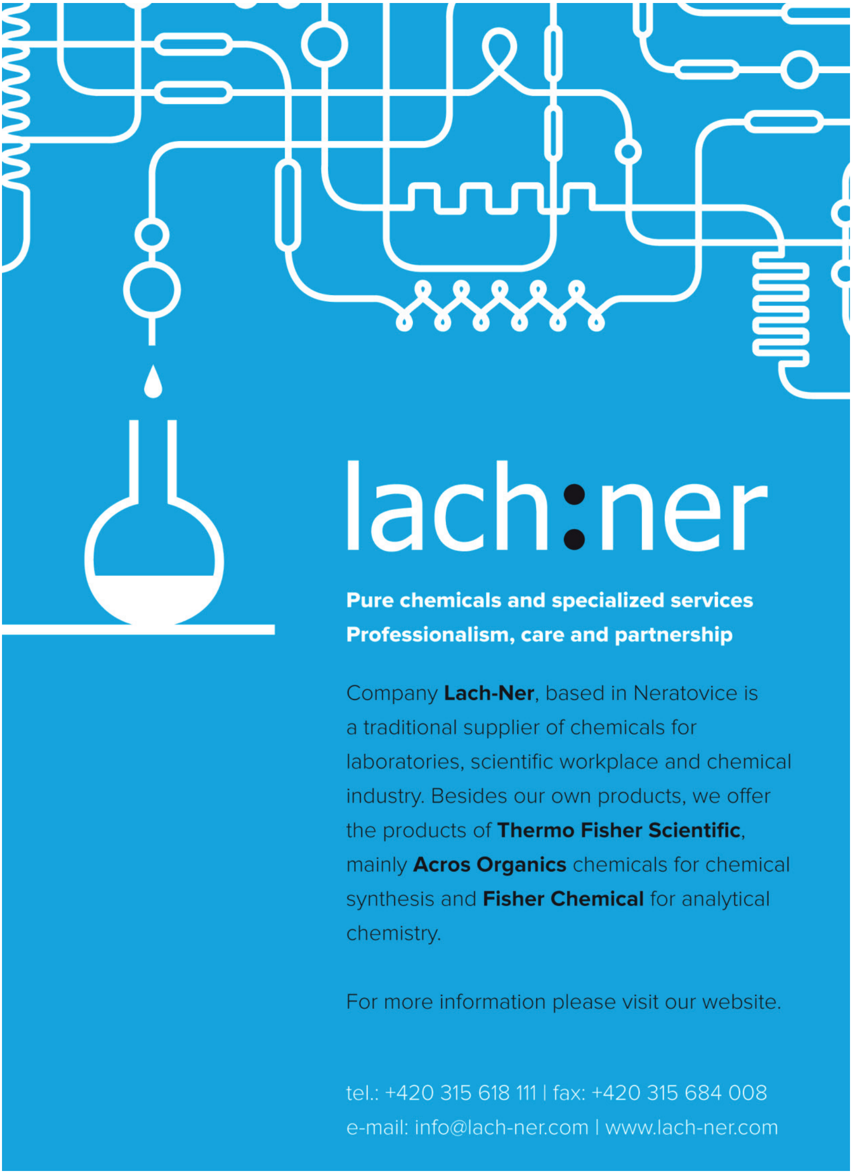

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Prague, July 2016

Self-assembly in the World of Polymers

Dear colleagues,

The understanding of self-assembly and self-organization in macromolecular systems is of crucial importance for the rational design of new functional materials for various technical and biomedical applications. The Conference *Self-assembly in the World of Polymers* aims at providing an international forum for reviewing and thorough discussion of the most recent approaches to these topics from the point of view of generation of self-assembled materials, investigation of their structure and properties, theoretical concepts of self-association and its modelling, and practical applications of self-organized systems in functional materials and biomedicine.

The Conference *Self-assembly in the World of Polymers* is also held to celebrate 99 years of the macromolecular concept first introduced in 1917 by Hermann Staudinger.

The Conference is the 80th in the series of *Prague Meetings on Macromolecules (PMM)*, the specialized conferences focused on various topical issues of polymer science. The PMM have been organized by the Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic under the auspices of the International Union of Pure and Applied Chemistry since the year 1967. During these years the PMM contributed greatly to promotion of professional networking, research collaboration, interdisciplinary education, and dissemination of our most recent scientific advances.

We believe that in addition to scientific programme also Prague as the Conference venue will be inspiring and exciting for you. You are welcome to join the guided tours on Wednesday afternoon to see the scenic areas of the Prague Castle and other magical places bearing more than 1000 years' history of the city and its dwellers.

We hope that you will enjoy the *80th PMM: Self-assembly in the World of Polymers* and wish you fruitful and mind refreshing days in Prague.

Petr Štěpánek
Conference Chairman

GENERAL INFORMATION

Venue

All sessions are held at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, Prague 6, Czech Republic.

Language

The official language of the conference is English.

Registration

On-site registration will take place on Sunday, 10 July 2016, from 16:00 to 19:00 at the Institute of Macromolecular Chemistry and will continue the next day from 8:00 to 16:00.

Please be aware that only persons wearing name badges received upon registration are entitled to enter the lecture rooms at the Institute.

PRESENTATIONS

The conference presentations will consist of main lectures and oral presentations. There will be two poster sessions, one on Monday 11 July and the other on Tuesday 12 July 2016.

Main lectures

are 40 minutes long, including questions and discussion.

Oral presentations

are 20 minutes long, including 5 minutes for questions and discussion.

Presentation files upload

We recommend that you upload your presentation at least one session ahead of your lecture.

IT administrator Mr Jiří Kaprálek will help you to upload and check your presentation. Please use your last name as the presentation file name.

Recordings

Audio/video recording of the lectures or copying of lecture files is not allowed without the prior consent of the speaker. The organizers reserve the right to capture photographs for documentation during the meeting.

Poster presentations

Materials for fixing posters will be provided on-site. Posters can be mounted at the beginning of each poster session and should be removed thereafter. The area reserved for mounting a poster is 200 cm high and 100 cm wide.

Poster sessions

- **Poster session I: Monday, 11 July 2016, 17:00 – 18:30**
  Posters P-01 – P-50
- **Poster session II: Tuesday, 12 July 2016, 16:50 – 18:30**
  Posters P-51 – P-99

Special poster contest

The scientific committee will evaluate posters from both poster sessions. The authors of the most interesting poster presentations will be announced at the Conference dinner and awarded by the chairman of the conference. Poster contest is kindly supported by journals ***ACS Macro Letters*** and ***Macromolecules***.

REFRESHMENTS AND LUNCHES

There will be coffee breaks each day. Lunch buffets will be open from Monday through Thursday in the dining hall of the Institute during the lunch breaks. The cost of refreshments and lunches is included in the conference fee as well as the welcome buffet and conference dinner.

SOCIAL EVENTS

The cost of the following social events are included in the conference fee. Accompanying guests can pay for the Wednesday afternoon programme and conference dinner at the registration desk.

Sunday, 10 July 2016

16:00 – 19:00 **Registration with welcome buffet**

Participants of the conference will be registered and equipped with the conference materials. Refreshments will be provided during registration, an occasion for having friendly talks with other guests of the conference.

Wednesday, 13 July 2016

Guided Tours in Prague

Guided tours will depart from the front of the Institute at 14:15 and will end in the city by 17:30.

1. Hradčany (Castle Town) Tour

Almost every visitor to Prague knows of the Prague Castle, but not everybody knows of Hradčany (until 1784 it was an independent "Castle Town"), a very interesting area surrounding the Castle. The tour will take you through the complex of the Strahov Monastery founded in the 12th century, and you will visit the interiors of Prague Loreto (which hosts an exact copy of the Italian "Santa Casa" chapel) and pass by glamorous noble palaces next to the small servants´ cottages. Finally, you can enjoy the relaxing part of the tour, the Castle moat in a friendly cool shadow.

2. Charles Bridge and Old Town Tour

The Charles Bridge is a unique historical sight renowned world-wide. It is undoubtedly one of Prague´s main cultural symbols. Let´s cross it and learn more about its history. Afterwards you will visit the Old Town (the oldest of four historical towns of Prague). The centre and main attraction of it is the Old Town Square with the Astronomical clock. The tour will finish at the art nouveau Municipal House and medieval Powder Tower. This route covers the Prague sightseeing highlights. You will learn a lot about the history of the place, but also some local legends...

3. Charles Bridge and Lesser Town Tour

This tour will take you through the Lesser Town, the second oldest historical town of Prague (founded in the 13th century). We will start by the specious baroque Wallenstein garden and then continue to the Charles Bridge and Kampa Island. After seeing the famous John Lennon Wall we will walk through local poetic streets that appeared also in the movie Amadeus. During the tour we will see some baroque palaces and also churches. Of course, we cannot miss the church with the miraculous „Infant of Prague“. Also this area is full of local legends, join the tour and listen to them...

4. Magical Prague

Prague is a very old city that enchants almost all of its visitors, mostly due to its beautiful architecture and preserved historical centre. However, have you ever visited its hidden corners, tiny narrow streets and secret passages? Doing so reveals more than the "ordinary" beauty of the city – it unfolds the city's magical power. Join this tour and learn about Prague‘s mysteries, fairy tales and legends. Visit places where scary ghosts may appear but also miraculous locations where people´s wishes come true...

19:00 Conference dinner at the Kaiserstein Palace

Malostranské náměstí 37/23

(one tram stop from Malostranská Metro station line A)

You are invited to discover the discreet charm of Baroque artwork in Prague's Lesser Quarter, the Kaiserstein Palace. Originally built in 1654, the palace is now protected as a historical landmark by UNESCO. The palace has had many famous dwellers over the years, such as opera diva Emmy Destinn and the scientist Joachim Barrande.

PRAGUE TRANSPORT

Public transport

A ticket for 24 Czech Crowns (CZK) is valid for a 30-min journey. A ticket for 32 CZK is valid for a 90-min journey by all means of public transport (trams, buses, metro and local trains) for an unlimited number of transfers. The 24-hour ticket costs 110 CZK. Tickets are sold at the airport, at railway and metro stations, at newspaper stands, at hotel reception desks, *etc*. The Metro runs from 5:00 till midnight.

We will provide those who have indicated an interest in the registration form with special conference transport tickets for reduced costs. If you are interested, please inquire at the conference transport corner near the registration desk.

Airport and railway stations

The Václav Havel Airport Prague is situated 9 km from the Institute, with a comfortable connection by bus No. 191 to/from the "Sídliště Petřiny" stop next to the Institute. International trains arrive at and depart mainly from the station Praha Hlavní nádraží (Metro red line C). **The Institute is situated near the Metro station "Petřiny", green line A.**

EMERGENCY PHONE NUMBERS

General emergency: 112
Medical ambulance service: 155
Police: 158

CONFERENCE PROGRAMME

Sunday, 10 July 2016

16:00 – 19:00 **Registration with welcome buffet**

Monday, 11 July 2016

9:00 – 9:10 **OPENING**
Jiří Kotek (Director of the Institute)
Petr Štěpánek (Conference Chairman)

9:10 – 9:20 **Presentation of IUPAC**
Pavel Kratochvíl *(Czech Republic)*

LECTURE SESSION 1

Chaired by: Petr Štěpánek (Czech Republic)

9:20 – 10:00 Main lecture ML-01
Timothy P. Lodge *(USA)*
Dynamics of chain exchange in block copolymer micelles

10:00 – 10:20 Oral presentation OP-01
Ilja K. Voets *(Netherlands)*
Using supramolecular handles to orchestrate polymer self-assembly

10:20 – 10:40 Oral presentation OP-02
Jens Gaitzsch *(Switzerland)*
Polypeptoids and polyesters as alternatives to methacrylic self-assemblies

10:40 – 11:10 Coffee break

LECTURE SESSION 2

Chaired by: Seunghwan Lee (Denmark)

11:10 – 11:50 Main lecture ML-02
Jean-François Lutz *(France)*
About sequences, codes and polymers

11:50 – 12:10 Oral presentation OP-03
Marcus Müller *(Germany)*
Process-directed self-assembly of block copolymer materials

12:10 – 12:30 Oral presentation OP-04
Petr Štěpánek *(Czech Republic)*
Probing protein fouling and DNA complexation with biocompatible block copolymers

12:30 – 14:00 *Lunch*

LECTURE SESSION 3

Chaired by: Jiří Pánek (Czech Republic)

14:00 – 14:40 Main lecture ML-03
Sébastien Lecommandoux *(France)*
Biomimetic compartmentalized polymersomes from controlled self-assembly of block copolymers

14:40 – 15:00 Oral presentation OP-05
Dietmar Appelhans *(Germany)*
Light- and pH-responsive polymersomes for synthetic biology

15:00 – 15:20 Oral presentation OP-06
Hannes Gumz *(Germany)*
Smart polymersomes: Tunable pH-sensitivity and enzyme encapsulation

15:20 – 15:50 *Coffee break*

LECTURE SESSION 4

Chaired by: Elise Deniau (France)

15:50 – 16:20 Main lecture ML-04
Andreas Walther *(Germany)*
Self-assemblies with programmable lifetimes and autonomously dynamic materials

16:20 – 16:40	Oral presentation OP-07 **Yingjie Liao** *(France)* Self-assembly of sugar-based block copolymers by solvent vapor annealing
16:40 – 17:00	Oral presentation OP-08 **Samuel Lörcher** *(Switzerland)* Self-organization of polymeric nano-compartments or nano-reactor-origami
17:00 – 18:30	**Poster Session I: Posters P-01 – P-50**

Tuesday, 12 July 2016

LECTURE SESSION 5

Chaired by: Cornelia G. Palivan (Switzerland)

9:00 – 9:40	Main lecture ML-05 **Christine M. Papadakis** *(Germany)* Physical hydrogels via charge driven self-organization of a triblock polyampholyte in dependence on charge asymmetry and ionic strength
9:40 – 10:00	Oral presentation OP-09 **Sergey Filippov** *(Czech Republic)* Novel triphilic block copolymers based on poly(2-methyl-2-oxazoline)-block-poly(2-octyl-2-oxazoline) with different terminal perfluoroalkyl fragments
10:00 – 10:20	Oral presentation OP-10 **Julien Bernard** *(France)* Highly ordered nanoporous films from supramolecular diblock copolymers with H-bonding junctions
10:20 – 10:40	Oral presentation OP-11 **Arianna Bartolini** *(Italy)* Encapsulation of small molecules by poly(ethylene glycol)-*graft*-poly(vinyl acetate) unimer micelles
10:40 – 11:10	*Coffee break*

LECTURE SESSION 6

Chaired by: Martin Hrubý (Czech Republic)

11:10 – 11:50	Main lecture ML-06 **Alexander V. Kabanov** *(USA)* Biomedical applications of nano-sized polyion complexes
11:50 – 12:10	Oral presentation OP-12 **Cornelia G. Palivan** *(Switzerland)* Polymer membranes decorated with proteins: Smart self-assembled functional nanosystems
12:10 – 12:30	Oral presentation OP-13 **Bo Örjan Gunnar Nyström** *(Norway)* Self-assembled structures of polymers for medical applications
12:30 – 14:00	*Lunch*

LECTURE SESSION 7

Chaired by: Marcus Müller (Germany)

14:00 – 14:40	Main lecture ML-07 **Oleg Borisov** *(Russian Federation)* Design principles of block copolymer nanostructures
14:40 – 15:00	Oral presentation OP-14 **Elena E. Dormidontova** *(USA)* Computer modeling of diblock copolymer self-assembly in solution: From dynamics to hydration
15:00 – 15:20	Oral presentation OP-15 **Karel Procházka** *(Czech Republic)* Computer study of the electrostatic co-assembly in non-stoichiometric mixtures of block polyelectrolytes
15:20 – 15:50	*Coffee break*

LECTURE SESSION 8

Chaired by: Stergios Pispas (Greece)

15:50 – 16:10	Oral presentation OP-16 **Peter Košovan** *(Czech Republic)* Coupling between ionization and conformation in pH-responsive polyelectrolytes
16:10 – 16:30	Oral presentation OP-17 **Remco Tuinier** *(Netherlands)* Prediction of polymeric self-assembly by self-consistent field computations
16:30 – 16:50	Oral presentation OP-18 **Alexander A. Yaroslavov** *(Russian Federation)* Complexes of cationic polymers with anionic liposomes
16:50 – 18:30	**Poster Session II: Posters P-51 – P-99**

Wednesday, 13 July 2016

LECTURE SESSION 9

Chaired by: Ilja K. Voets (Netherlands)

9:00 – 9:40	Main lecture ML-08 **Axel H. E. Müller** *(Germany)* Self-organized multicompartment nanostructures of ABC triblock terpolymers inspired by the cell
9:40 – 10:00	Oral presentation OP-19 **Corinne C. Nardin** *(France)* Self-assembling biohybrid materials
10:00 – 10:20	Oral presentation OP-20 **Stergios Pispas** *(Greece)* Effect of lysozyme complexation on the thermoresponsive behavior of PnBA-b-PNIPAM-COOH micellar aggregates

10:20 – 10:40	Oral presentation OP-21 **Martin Hrubý** *(Czech Republic)* Seven years of radionuclide laboratory at the Institute of Macromolecular Chemistry AS CR – important achievements
10:40 – 11:10	*Coffee break*

LECTURE SESSION 10

Chaired by: Sergey Filippov (Czech Republic)

11:10 – 11:50	Main lecture ML-09 **Jean-François Gérard** *(France)* Nanostructured thermosets from self-assembling processes
11:50 – 12:10	Oral presentation OP-22 **Tomaz Einfalt** *(Switzerland)* Towards stimuli responsive artificial cell organelles by biomimetic engineering of complex membrane processes
12:10 – 12:30	Oral presentation OP-23 **Yue Zhao** *(Canada)* CO_2-stimulated shape and morphological transitions of block copolymer assemblies
12:30 – 12:50	Oral presentation OP-24 **Adem Levend Demirel** *(Turkey)* Self-assembly of poly(2-alkyl-2-oxazoline)s in aqueous solutions
12:50 – 14:15	*Lunch*
14:15 – 17:30	**Social programme (Guided tour in Prague)**
19:00 – 22:00	**Conference dinner**

Thursday, 14 July 2016

LECTURE SESSION 11

Chaired by: Corinne Nardin (France)

9:00 – 9:40	Main lecture ML-10 **Walter Richtering** *(Germany)* Self-assembly of soft microgels in bulk and at interfaces
9:40 – 10:00	Oral presentation OP-25 **Seunghwan Lee** *(Denmark)* Hydrophilic polymer brushes spontaneously formed as segregated from silicone matrix at the interface with water
10:00 – 10:20	Oral presentation OP-26 **Sabrina Belbekhouche** *(France)* Promising tailor made hollow chitosan/poly(acrylic acid) nanoparticles for antibiotic therapy
10:20 – 10:40	Oral presentation OP-27 **Patrick Lacroix-Desmazes** *(France)* Supramolecular self-assembly of double hydrophilic block copolymers and their use as structure-directing agents for the synthesis of drug-loaded ordered mesoporous silica
10:40 – 11:10	*Coffee break*

LECTURE SESSION 12

Chaired by: Bo Örjan Gunnar Nyström (Norway)

11:10 – 11:50	Main lecture ML-11 **Matthias Ballauff** *(Germany)* Self-assembly of proteins and polyelectrolytes: Comparing experiments to theory and simulations
11:50 – 12:10	Oral presentation OP-28 **Christophe Schatz** *(France)* Stopped-flow study of macromolecular assemblies of polyelectrolytes

12:10 – 12:30	Oral presentation OP-29 **Elise Deniau** *(France)* Self-organization of cationic pH- and thermo-responsive copolymers
12:30 – 14:00	*Lunch*

LECTURE SESSION 13

Chaired by: Karel Procházka (Czech Republic)

14:00 – 14:40	Main lecture ML-12 **Spiros H. Anastasiadis** *(Greece)* Effects of spatial confinement on polymer structure and dynamics
14:40 – 15:00	Oral presentation OP-30 **Wei Sun** *(People's Republic of China)* Exploration of selective decoration of Janus silica particles within polymeric patterned pore arrays
15:00 – 15:20	Oral presentation OP-31 **Christian Rossner** *(Germany)* Planet-satellite nanostructures from star polymers and gold nanoparticles
15:20 – 15:40	Oral presentation OP-32 **Roey Jacob Amir** *(Israel)* Spectrally active polymeric micelles
15:40 – 16:00	Oral presentation OP-33 **Daniela Täuber** *(Sweden)* Two-dimensional polarization microscopy reveals polymer chain self-organization in thin films of conjugated polymers
16:00	***Closing of the Meeting, FAREWELL***

LIST OF POSTERS

P-01

S. M. Lee, J. Y. Lee, B. J. Kim, K. Y. Choi, K. M. Lee, **J. C. Lim**
(Republic of Korea)
Synthesis of polymeric biosurfactants from vegetable oils and characterization of interfacial properties for cosmetic products

P-02

F. Laffleur *(Austria)*
The next generation of mucoadhesive biopolymers

P-03

V. V. Vasilevskaya, A. A. Glagoleva *(Russian Federation)*
Intramolecular segregation within amphiphilic macromolecules: Cylinders & vesicle

P-04

N. Tiwari, P. van der Schoot *(Netherlands)*
Stochastic lag time in nucleated linear self-assembly

P-05

P. Fiurasek, T. van de Ven, A. Soldera *(Canada)*
Quebec Center for Advanced Materials (QCAM)

P-06

S. Gupta, P. Chokshi *(India)*
Interparticle interactions between diblock copolymer grafted nanosheets

P-07

D. C. Leite, T. Hellweg, **N. P. da Silveira** *(Brazil)*
Starch based nanoparticles

P-08

S. Schoettner, H.-J. Schaffrath, M. Gallei *(Germany)*
Preparation of porous functional films by microphase separation of block copolymers

P-09

Y.-W. Kim *(Republic of Korea)*
Micro-phase separation of renewable multiarm block copolymers for thermoplastic elastomers

P-10

E. Tomšík, N. Shevchenko, G. Pankova, T. Ukleev, A. Sel’kin
(Czech Republic)
Monodisperse polymeric particles: Self-assembling and luminescence properties

P-11

E. Tomšík, N. Gospodinova *(Czech Republic)*
Self-assembled highly ordered poly(3,4-ethylenedioxythiophene) films with high electrochemical capacitance and electrochromic efficiency

P-12

S. Schmidt, P. Vana *(Germany)*
Microphase separation of novel amphiphilic multiblock copolymers

P-13

E. Konishcheva, W. Meier *(Switzerland)*
PEG-b-PCL diblock copolymers: Optimization of the synthesis towards low PDI for targeted self-assembled structures

P-14

H.D.M. Follmann, O. N. Oliveira Jr, R. Silva, T. Asefa
(United States of America)
Hybrid hyperbranched polymer/mesoporous silica for prolonged drug delivery

P-15

J. Labuta, N. Velychkivska, L. Starovoytova, M. Hrubovský, H. Kouřilová, L. Hanyková, I. Krakovský, J. Lang, S. Ishihara, J. P. Hill *(Japan)*
Phase separation in water soluble porphyrin/polymer hybrid systems

P-16

D. G. Angelescu, D. Caragheorgheopol *(Romania)*
Assembly of virus-like nanoparticles in presence of a flexible polyion.
A molecular dynamics simulation investigation

P-17

C. Cîrtoaje, C. Stan, E. Petrescu *(Romania)*
Cobalt ferrite nanoparticles in nematic liquid crystals

P-18
C. Cîrtoaje, E. Petrescu *(Romania)*
Aligned nanoparticles in nematic liquid crystals

P-19
N. A. Obraztsova, S. V. Kurmaz *(Russian Federation)*
Amphiphilic branched copolymers of N-vinylpyrrolidone – a promising drug carriers

P-20
A. F. Khusnuriyalova, A. V. Sykhov, E. V. Gorbachuk, R. I. Vagizov, D. G. Yakhvarov *(Russian Federation)*
Electrochemical generation of transition metal nanoparticles (Fe, Co, Ni) for catalytic oligo- and polymerization

P-21
T.-H. Chen, Y.-T. Tseng, C.-H. Chen, H.-T. Chang *(Taiwan)*
Strategies for formation of various superstructures of carbon dots

P-22
P. Kratochvíl, **M. Netopilík** *(Czech Republic)*
The effect of nanoparticle non-uniformity on the ratio of radius of gyration and hydrodynamic radius

P-23
L. Nová, F. Uhlík, P. Košovan *(Czech Republic)*
Molecular simulations of flower-like micelles and micellar gels

P-24
L. Nová, P. Košovan, F. Uhlík *(Czech Republic)*
pH-responsive behaviour of linear weak polyelectrolyte

P-25
A. Kuriata, **A. Sikorski** *(Poland)*
The structure of cyclic multiblock copolymers

P-26
J. Gaitzsch, V. Chudasama, G. Battaglia, W. Meier *(Switzerland)*
Biomimetic polymersomes through a symbiosis of organic and polymer chemistry

P-27
H. J. Lee, D. E. Kim, **S. C. Lee** *(Republic of Korea)*
Mineralized assembled nanoparticles for nitric oxide-mediated cancer therapy

P-28
L. Suchá, Z. Limpouchová, K. Procházka *(Czech Republic)*
Conformational behaviour of polymer chains of different architectures in solvent mixtures. Dissipative particle dynamics study

P-29
N. Gospodinova, T. Skorokhoda, O. Kohut, E. Tomšík *(Czech Republic)*
Self-assembled liquid-crystalline and nano-crystalline structures of polyaniline: Spectral and electrochromic signatures

P-30
J. Choi, A. Kirakosyan, J. Im *(Republic of Korea)*
Self-assembly of polymer grafted nanoparticles for "matrix-free" polymer nanocomposites

P-31
K. Šindelka, Z. Limpouchová, L. Suchá, K. Procházka *(Czech Republic)*
Solubilisation of linear homopolymer chains into electrostatically co-assembled micelles. A dissipative particle dynamics study

P-32
C. D. Bösch, S. M. Langenegger, R. Häner *(Switzerland)*
Self-assembly of phenanthrene oligomers into nanotubes with light-harvesting properties

P-33
J.-C. Chang, E. Amstad *(Switzerland)*
Food-grade capsules based on microfluidic

P-34
R. Konefał, J. Spěváček *(Czech Republic)*
NMR study of two types of thermoresponsive polymer systems in aqueous media

P-35
R. Schlegel, H. Budde, U. Wendler, M. Bartke, M. Beiner *(Germany)*
Mechanical properties of multigraft copolymers prepared by an up-scalable synthesis approach

P-36
R. Schlegel, N. Mahmood, H. Budde, U. Wendler, M. Beiner *(Germany)*
Enhancement of tensile strength of multigraft copolymers - influence of blending and peroxide cross-linking

P-37
A. Zhigunov, P. Matějíček, A. Kuklin, Yu. S. Kovalev *(Czech Republic)*
Aggregation behavior of sodium dodecaborate

P-38
O. Boytsova, A. Sadovnikov, A. J. Sutherland *(United Kingdom)*
Self-assembly formation of NH_4TiOF_3 mesocrystals: Control shape and sizes via length and ratio of poly(ethylene glycol)s

P-39
V. H. Fragal, E. H. Fragal, A. F. Rubira, **R. Silva** *(Brazil)*
Self-organization of two-dimensional nanopores and their use in cell growth and plasmonics

P-40
E. N. Govorun, A. V. Chertovich *(Russian Federation)*
Self-assembly of random multiblock copolymers: Effect of short block penetration into "alien" domains of the lamellar phase

P-41
J. Yan, J. Cao, B. He *(People's Republic of China)*
Nanocarriers self-assembled from functionalized polyethylenimine for anticancer drug delivery

P-42
Y. Zhang, X. Peng, S. Li, B. He *(People's Republic of China)*
Polymeric micelles with different topological architectures for drug delivery

P-43
K. J. Jang, S. E. Hong, R. K. R. Yoon *(Republic of Korea)*
Fabrication of flexible cellulose films containing marine organisms

P-44
X. Peng, Y. Zhang, Y. Chen, B. He *(People's Republic of China)*
Synthesis and self-assembly of biodegradable miktoarm star copolymers μ-PEG-PCL-PLLA

P-45
M. Peksa, S. Burrekaew, R. Schmid, F. Stallmach, **J. Lang** *(Czech Republic)*
NMR diffusion and relaxation techniques and MD simulation – powerful toolbox to describe binding and motions of the guest in an anisotropic metal-organic framework

P-46
A. V. Romanyuk, I. D. Grozdova, N. S. Melik-Nubarov *(Russian Federation)*
Pluronic-based chemiluminescent emulsion as a novel agent for antitumor therapy

P-47
A. V. Romanyuk, I. D. Grozdova, N. S. Melik-Nubarov, H. Frey *(Russian Federation)*
Control of cell viability and multidrug resistance by amphiphilic nonionic block copolymers

P-48
L. Xu, W. Gao, B. He *(People's Republic of China)*
Self-assembly of L-phenylalanine based dipeptide low molecular weight gel for chemotherapy

P-49
M. Marudova, I. Bodurov, S. Sotirov, Y. Uzunova, B. Pilicheva, A. Viraneva, I. Vlaeva, G. Exner, T. Yovcheva *(Bulgaria)*
Layer-by-layer self-assembly of polyelectrolyte multilayers on biodegradable substrates with respect to controlled drug release

P-50
L. Loukotová, M. Hrubý *(Czech Republic)*
Thermoresponsive β-glucan-based polymers for biomedical applications

P-51
M. Holubová, M. Hrubý *(Czech Republic)*
Nanospecies affecting amyloid formation

P-52

M. Rabyk, E. Deniau, L. Billon, O. Borisov, M. Hrubý, P. Štěpánek
(Czech Republic)
Novel amphiphilic block-gradient copolymers of styrene and 2-dimethylaminoethyl acrylate

P-53

A. S. Gubarev, N. V. Tsvetkov, E. V. Lebedeva, A. A. Lezov, M. E. Mikhailova, L. I. Akhmadeeva, N. V. Kuchkina, E. S. Serkova, Z. B. Shifrina *(Russian Federation)*
The conformational and hydrodynamic parameters of novel hyperbranched pyridylphenylene polymers

P-54

N. V. Tsvetkov, A. A. Lezov, **A. S. Gubarev**, E. V. Ubyivovk, N. V. Girbasova, A. Y. Bilibin *(Russian Federation)*
The study of argentum nanoparticles stabilized with modified PEG

P-55

L. Kratofil Krehula, S. Krehula, V. Gilja, A. Husak, M. Perlog, J. Stjepanović, S. Šuka, Z. Hrnjak-Murgić *(Croatia)*
Synthesis, characterization and photocatalytic activity of polypyrrole/TiO_2 and polypyrrole/ZnO composites

P-56

A. Markina, V. Ivanov, P. Komarov, A. Khokhlov, S.-H. Tung
(Russian Federation)
Self-organization processes in lecithin-bile salt mixtures: Computer simulation

P-57

A. Markina, V. Ivanov, P. Komarov, S. V. Larin, S. V. Lyulin
(Russian Federation)
Coarse-grained computer simulation of crystallization in polyimide melts

P-58

J. Tian, P. Vana *(Germany)*
Preparation and self-assembly of amphiphilic hybrid polymer/gold nanoparticles at liquid-liquid interface

P-59

S. E. Hong, K. J. Jang, K. R. Yoon *(Republic of Korea)*

Formation of surface modified core/shell(Fe_3O_4@SiO_2) nanoparticles of CD(β-Cyclodextrin) for detect and separation of dyes

P-60

M. Icli Ozkut *(Turkey)*

Another step to zero band gap plastics: A soluble, low band gap bisthiadiazole based electrochromic polymer

P-61

G. Gokce, B. Karabay, A. Cihaner, M. Icli Ozkut *(Turkey)*

Acid/ base doped/ dedoped low band gap polymer

P-62

W. T. Chuang, Y. M. Hsu, Y. S. Sun, U. S. Jeng *(Taiwan)*

Successive use of cylinder-forming dendron-jacketed block copolymers as templates for synthesis of nanostructured mesoporous TiO_2/carbon films

P-63

J. Kim, J. H. An, J. Y. Bae, D. J. Chung, S. H. Kim *(Republic of Korea)*

Effect of epoxy structures on thermal conductivities of liquid crystalline epoxy/alumina composites

P-64

J. H. Ye, S. H. Choi *(Republic of Korea)*

Combustion characteristics of flame retardants based on poly(phosphoric acid ester)

P-65

A. V. Sybachin, O. V. Zaborova, T. J. Deming, A. A. Yaroslavov
(Russian Federation)

Biodegradable nanocontainers composed of anionic liposomes and cationic polypeptide vesicles

P-66

X. Wang, Z. Limpouchová, M. Lísal, K. Procházka *(Czech Republic)*

Effect of solvent quality on the chromatographic separation of linear and H-shaped polymers: A Monte Carlo study

P-67

F. Delisavva, M. Uchman, J. Škvarla, E. Wozniak, E. Pavlova, M. Šlouf, V. Garamus, K. Procházka, M. Štěpánek *(Czech Republic)*

Influence of corona structure on binding of an ionic surfactant in oppositely changed amphiphilic polyelectrolyte micelles

P-68

T. Erşen Dudu, D. Alpaslan, N. Aktas *(Turkey)*

Environmentally friendly superabsorbent polymers for water-holding in agricultural lands and their application for environmental purposes

P-69

T. Erşen Dudu, **D. Alpaslan**, N. Aktas *(Turkey)*

Synthesis, characterization and possible agricultural application of nonionic p(DMAAm) hydrogel

P-70

T. Erşen Dudu, **D. Alpaslan**, N. Aktas *(Turkey)*

Characterization of cationic hydrogels and their removal of phenol red textile dyes from aqueous environment

P-71

E. Karpushkin, L. Lopatina, V. Sergeyev *(Russian Federation)*

Decoration of DNA scaffold by gold nanoparticles formed in aqueous solutions

P-72

J. Pánek, E. Koziolová, P. Štěpánek, T. Etrych, O. Janoušková *(Czech Republic)*

Fluorescence lifetime imaging of polymer therapeutics

P-73

O. Sedláček, D. Jirák, A. Galisová, M. Hrubý *(Czech Republic)*

Dual-responsive injectable polymer depots visualizable by 19F-MRI

P-74

E. Jäger, A. Höcherl, A. Jäger, M. Hrubý, O. Janoušková, R. Konefał, M. Netopilík, J. Pánek, M. Šlouf, K. Ulbrich, P. Štěpánek *(Czech Republic)*

Polymer nanoparticles with reactive oxygen species (ROS)-triggered cargo release for drug-delivery applications

P-75
A. Jäger, E. Jäger, M. Hrubý, R. Konefał, Z. Syrová, T. Mazel, D. Cmarko, I. Raška, P. Štěpánek *(Czech Republic)*
Pegylated polyester nanoparticles for delivery of paclitaxel: Synthesis, characterization and *in vitro* studies

P-76
M. Kownacki, S. M. Langenegger, R. Häner *(Switzerland)*
Efficient light-harvesting antenna through the intermediate donor-acceptor pyrene derivative

P-77
T. P. T. Dao, F. Fernandes, K. Ferji, M. Prieto, O. Sandre, **J. F. Le Meins** *(France)*
Controling membrane structure of hybrid polymer/lipid giant unilamellar vesicles

P-78
T. P. T. Dao, F. Fernandes, K. Ferji, M. M. Er-Rafik, M. Schmutz, M. Prieto, O. Sandre, **J. F. Le Meins** *(France)*
Towards the control of nanodomain formation in large hybrid polymer/lipid unilamellar vesicles (LHV)

P-79
T.-H. Kim, E. Kim, C. Do, H. Ahn, Y.-S. Han *(Republic of Korea)*
Controllable self-assembly of block copolymers in aqueous solution: A small angle scattering study

P-80
P. Ai, H. Y. Xion *(People's Republic of China)*
Chiral separation of D,L-metoprolol through cellulose mixed membranes

P-81
Y. M. Bi, P. L. Xu, G. Tang, F. X. He, D. You, F. Lin *(People's Republic of China)*
Self-assembled micelles of poly(vinyl acetate)-b-poly(N-vinyl caprolactum) for temperature-triggered drug delivery

P-82
C. Yuan, Q. Ruan, S. M. Chi, P. Zheng, **Y. Zhao** *(People's Republic of China)*
Host–guest supramolecular system of RZK anti-HIV agent and β-cyclodextrin

P-83

S. Ehrmann, B. N. S. Thota, R. Haag *(Germany)*
Comparison of steroid- and alkyl-based dendritic amphiphiles for drug encapsulation

P-84

E. Altınkaya, Y. Seki, B. O. Gürses, O. C. Yılmaz, M. Sarıkanat, L. Çetin, O. Özdemir, İ. Şen, K. Sever *(Turkey)*
Effect of pDADMAc concentration on electromechanical performance of chitosan-based electroactive actuators

P-85

D. Zeini, J. Glover, B. Nyström *(Norway)*
Application of light activated lysine grafted dextran nanoparticles for targeted si-RNA delivery in neuroscience

P-86

A. Riabtseva, L. Kaberov, J. Kučka, M. Hrubý, S. Filippov *(Czech Republic)*
Novel pH-sensitive nanocontainers based on Eudragit/Brij98 mixture for oral drug delivery

P-87

R. K. Donato, E. Jäger, A. Jäger, A. Höcherl, V. Z. Bergamo, A. M. Fuentefria, M. G. Raucci, L. Ambrosio, P. Štěpánek *(Brazil)*
Biodegradable and biocompatible polymer nanoparticles with fungal biofilm inhibition and mesenchymal stem cell growth capabilities

P-88

K. Z. Donato, R. K. Donato, M. Lavorgna, L. Ambrosio, H. S. Schrekker, R. S. Mauler *(Brazil)*
Biocompatible HAVOH/silica/ionic liquid hybrid's interface bonding

P-89

D. Aycan, N. Alemdar *(Turkey)*
Chitosan-based hydrogel with a high water uptake capacity for biomedical applications

P-90

T.-H. Chen, **W.-L. Tseng** *(Taiwan)*
Concentration-modulation of self-assembly of monodisperse carbon dots: Formation of high-brightness nanoaggregates with full-color emission

P-91
V. Mikhalevich, C. Draghici, J. Kowal, G. Gunkel-Grabole, W. Meier, C. G. Palivan *(Switzerland)*
"Active surfaces": Biomolecule - polymer membranes for efficient sensing of phenols

P-92
M. Garni, M. Lomora, T. Einfalt, F. Itel, A. Dinu, W. Meier, C. G. Palivan *(Switzerland)*
Biopores inside synthetic membranes of giant unilamellar vesicles (GUVS)

P-93
A. Gavrilov, A. Chertovich *(Russian Federation)*
Self-assembly in polyelectrolyte melts: Mesoscale simulation

P-94
O. V. Zaborova, S. Filippov, P. Chytil, T. Etrych *(Czech Republic)*
Self-assembly of liposomes coated with amphiphilic HPMA-based copolymers

P-95
T. Nejedlý, J. Trousil, M. Hrubý, Z. Walterová, M. Šlouf *(Czech Republic)*
Self-assembly of chloroxine into crystalline nanoparticles for Wilson's disease treatment

P-96
D. Bozoğlu, **D. Değer**, H. Deligöz, K. Ulutaş *(Turkey)*
Dielectric properties of silica aerogel/polyvinylidene fluoride (PVDF) composites

P-97
E. Ozturk, T. Gürkaynak, H. Deligöz, M. Acikgoz, **D. Değer** *(Turkey)*
Preparation and electrical behavior of oleic acid coated $CoFe_2O_4$ nanoparticles doped into polyester composite films

P-98
S. Yakut, D. Değer, **K. Ulutaş** *(Turkey)*
Plasma discharge power dependent alternative conductivity of plasma polymerized polyethylene oxide (pPEO) thin films

P-99

J. Trousil, J. Matějková, S. Filippov, Z. Syrová, T. Mazel, S. Svidenská, L. Kováčik, D. Cmarko, M. Hrubý, R. Lund, B. Nyström, I. Raška, P. Štěpánek *(Czech Republic)*

Antituberculotic rifampicin drug delivery system based on polyester nanoparticles

NOTES

MAIN LECTURES

ML-01

DYNAMICS OF CHAIN EXCHANGE IN BLOCK COPOLYMER MICELLES

T. P. Lodge[a,b], E. Wang[b], Y. Ma[a], F. S. Bates[b]

[a]*Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA*

[b]*Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455, USA*

(lodge@umn.edu)

Block copolymers provide a versatile platform for achieving desired nanostructures by self-assembly. In particular, block copolymer micelles in selective solvents are of interest across a range of technologies, including drug delivery, imaging, catalysis, lubrication, and extraction. While block copolymers generally adopt the morphologies familiar in surfactants and lipids (*i.e.*, spherical micelles, worm-like micelles, and vesicles), one key difference is that polymeric micelles are typically not at equilibrium. The primary reason is the large number of repeat units in the insoluble block, N_{core}, which makes the thermodynamic penalty for extracting a single chain ("unimer exchange") substantial. As a consequence, the critical micelle concentration (CMC) is rarely accessed experimentally; however, in the proximity of a critical micelle temperature (CMT), equilibration is possible. We use time-resolved small angle neutron scattering (TR-SANS) to obtain a detailed picture of the mechanisms and time scales for chain exchange, at or near equilibrium. One model system is poly(styrene-*b*-(ethylene-*alt*-propylene)) (PS-PEP), in the PEP-selective solvent squalane ($C_{30}H_{62}$). Equivalent micelles with either normal (hPS) or perdeuterated (dPS) cores are initially mixed in a blend of isotopically substituted squalane, designed to contrast-match a 50:50 hPS:dPS core. Samples are then annealed at a target temperature, and chain exchange is revealed quantitatively by the temporal decay in scattered intensity. A second system consists of poly(n-butyl methacrylate)-*b*-poly(methyl methacrylate) in an ionic liquid. The rate of exchange as a function of concentration, temperature, N_{core}, N_{corona}, and chain architecture (diblock versus triblock) will be discussed.

ML-02

ABOUT SEQUENCES, CODES AND POLYMERS

J.-F. Lutz

Precision Macromolecular Chemistry, Institut Charles Sadron, 23 rue du Loess, 67034 Strasbourg, France
(jflutz@unistra.fr, https://www-ics.u-strasbg.fr)

Information-containing macromolecules are polymers that contain a message encrypted in their comonomer sequences. The archetypal example of such a polymer is DNA, which is used in biology to store genetic information.[1] However, DNA is certainly not the only polymer that can contain molecular information.[2] In principle, a string of information can be created in any copolymer using two comonomers defined intentionally as 0-bit and 1-bit. However, such polymers have to be monodisperse and perfectly sequence-defined. In addition, the message encoded in their chains should be easily read.

In this lecture, I will present recent achievements obtained in my laboratory for the synthesis of information-containing macromolecules. Recent progress in the field of sequence-controlled polymers allows synthesis of unnatural macromolecules with precisely controlled primary and secondary structures.[3-6] Uniform sequence-defined polymers can be prepared for example using orthogonal iterative strategies.[7] Furthermore, the readability of these polymers will be presented. For instance, the analysis of unnatural polymers by nanopore sequencing and tandem mass spectrometry will be discussed.

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ML-03

BIOMIMETIC COMPARTMENTALIZED POLYMERSOMES FROM CONTROLLED SELF-ASSEMBLY OF BLOCK COPOLYMERS

S. Lecommandoux

Laboratoire de Chimie des Polymères Organiques, LCPO-ENSCBP, UMR CNRS, Université de Bordeaux, 16 avenue Pey Berland, 33607 Pessac cedex, France.
(lecommandoux@enscbp.fr, www.lcpo.fr)

Polymersomes are among the most attractive systems for drug delivery applications. We report here an overview on the self-assembly in water of amphiphilic block copolymers into polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules. We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles. These copolymers that mimic the structure and function of glycoproteins represent an example of the effectiveness of a biomimetic strategy in implementing materials design. Finally our recent advances in using “biomimicry approaches” to design complex, compartmentalized materials will be proposed. Such a system constitutes a first step towards the challenge of structural cell mimicry and functionality.

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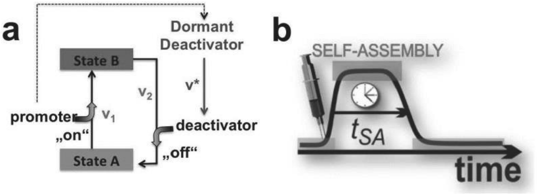
ML-04

SELF-ASSEMBLIES WITH PROGRAMMABLE LIFETIMES AND AUTONOMOUSLY DYNAMIC MATERIALS

A. Walther, T. Heuser, L. Heinen

DWI-Leibniz Institute for Interactive Materials, Aachen, Germany
(walther@dwi.rwth-aachen.de)

We present a generic concept to program lifetimes of self-assemblies in closed systems.[1-3] The key concept relies on separating the kinetic steps of formation and destruction of self-assemblies by controlling the availability of chemicals needed (i) to promote the assembly from the disassembled state A to the self-assembled state B (promoter) and (ii) its subsequent decay (deactivator; from B to A, Scheme 1). We conceive dormant deactivators that slowly chemically degrade, or are activated by introduction of the promoter, to furnish the active deactivator. The combination of fast promoters and dormant deactivators in a single injection enables a unique kinetic balance to establish an autonomously self-regulating, transient pH-state. Coupling of this non-equilibrium state to fuel pH-switchable self-assemblies allows predicting their assembly/disassembly fate in time - similar to a precise self-destruction mechanism. The duration of this transient state can be tuned over four orders of magnitude – from minutes to days – and gives rise towards autonomously dynamic and self-regulating material systems.



Scheme 1. Kinetic control to program self-regulating self-assemblies in time by combination of rapid promoters and dormant deactivators. The time scales can be programmed by controlling v* and the ratio of promoter/dormant deactivator.

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ML-05

PHYSICAL HYDROGELS VIA CHARGE DRIVEN SELF-ORGANIZATION OF A TRIBLOCK POLYAMPHOLYTE IN DEPENDENCE ON CHARGE ASYMMETRY AND IONIC STRENGTH

M. A. Dyakonova[a], N. Stavrouli[b], M. T. Popescu[b], A. V. Berezkin[a],
K. Kyriakos[a], S. K. Filippov[c], P. Štěpánek[c],
C. Tsitsilianis[b], C. M. Papadakis[a]

[a]*Technische Universität München, Physik-Department, James-Franck-Str. 1, 85748 Garching, Germany*

[b]*University of Patras, Department of Chemical Engineering, 26504 Patras, Greece*

[c]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*
(papadakis@tum.de, www.softmatter.ph.tum.de)

Physical hydrogels from the triblock polyampholytes PAA-P2VP-PAA and PAA-QP2VP-PAA (PAA, P2VP and QP2VP are poly(acrylic acid), poly(2-vinylpyridine) and quaternized poly(2-vinylpyridine)) are of interest as injectable hydrogels. We have investigated the rheological and structural properties of such hydrogels, formed via charge driven self-association of the oppositely charged blocks [1,2]. Small-angle neutron scattering (SANS, Figure 1) investigations revealed the morphologies in dependence on the charge asymmetry and the ionic strength and is compared to the rheological behavior and computer simulations.

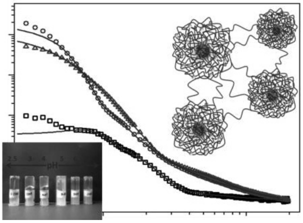

Figure 1. Photographs and SANS curves of PAA-QP2VP-PAA at different pH values along with a sketch of the structure at low pH.

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ML-06

BIOMEDICAL APPLICATIONS OF NANO-SIZED POLYION COMPLEXES

A. Kabanov[a,b]

[a]*University of North Carolina at Chapel Hill, 125 Mason Farm Road Chapel Hill, NC 27599-7362 USA*

[b]*M.V. Lomonosov Moscow State University, Moscow 117298, Russian Federation, kabanov@email.unc.edu*

The primary focus of this lecture will be the discussion of the chemistry, characterisation and applications of nanoscale size polyion complexes formed by ionic block copolymers and polypeptides for the delivery of these polypetides to the body. Examples include delivery of antioxidant enzymes (e.g. superoxide dismutase, catalase), stoichiometric and catalytic scavengers of organophosphorous toxins (butirylcholine esterase, organophosphate hydrolase) and neurotrophins (brain-derived neurotrophic factor, glial cell line-derived neurotrophic factor). The applications include treatments of obesity, stroke, Parkinson's disease, RETT syndrome, organophosphorous toxins poisoning, and some others medical conditions that have been demonstrated using animal models.

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ML-07

DESIGN PRINCIPLES OF BLOCK COPOLYMER NANOSTRUCTURES

O. V. Borisov[a,b,c]

[a]*Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR 5254 CNRS UPPA, Pau, France*
[b]*Institute of Macromolecular Compounds of the Russian Academy of Sciences, St.Petersburg, Russia*
[c]*St. Petersburg National University of Information Technologies, Mechanics and Optics, Russia*
Oleg.Borisov@univ-pau.fr

The most important requirements for applications of self-assembled block copolymer nanostructures in nanotechnology and in biomedicine are (i) precise control of size and morphology of the self-assembled structures over multiple length scales, (ii) robustness of fabrication and (iii) pronounced stimuli-responsive properties, which are the ability of a triggered response to varied external conditions or recognition of specific stimuli. We discuss how the desired properties of the polymer nanostructures can be rationally encoded into macromolecular architecture of the building blocks.

First, we demonstrate how the various generic morphologies of self-assembled nanostructures can be obtained by varying molecular architecture, e.g., replacing conventional linear diblock copolymers by miktoarm starlike, linear-cyclic and linear-dendritic block copolymers. These design principles are further applied to triblock terpolymers, where introducing of the third chemically different block allows extending dramatically the spectrum of possible morphologies of the nanostructures as compared to those formed by diblock copolymers. Here we consider both corona- and core-compartmentalized nano-assemblies formed by terpolymers with either one or two insoluble blocks.

Then we discuss responsive behaviour of self-assembled amphiphilic copolymer nanostructures, that is, capability of changing the morphology upon variation in temperature, ionic strength or pH of the solution. In the case of copolymer comprising weak polyelectrolyte blocks the interplay of copolymer association with ionization leads to most sophisticated assembly scenarios. Finally, we consider examples of stimuli-unduced intramolecular nanoscale organization and formation of unimolecular micelles in star-like and comb-shape (bottlebrush) block copolymers.

ML-08

SELF-ORGANIZED MULTICOMPARTMENT NANOSTRUCTURES OF ABC TRIBLOCK TERPOLYMERS INSPIRED BY THE CELL

Axel H. E. Müller

Institute of Organic Chemistry, Johannes Gutenberg Universität Mainz, Germany

Compartmentalization is the most important feature in living organisms, best seen in plant or animal cells, where different compartments have different functions. We aim at mimicking nature in synthesizing multicompartment micelles, which simultaneously can host different payloads, such as drugs or magnetic or fluorescent nanoparticles. The self-assembly of ABC triblock terpolymers in solution and in the bulk are ideally suited for such a task.

We have prepared corona-compartmentalized nanoparticles (Janus spheres, cylinders, or disks) by crosslinking domains in the bulk nanostructures of triblock terpolymers. These Janus micelles have superior properties as interfacial agents, as stabilizers in emulsion polymerization, as compatibilizers of polymer blends, or for the solubilization of carbon nanotubes.

Here we present a flexible route for the hierarchical, guided self-assembly of triblock terpolymers into multicompartment micelles (MCMs) of different shapes and sizes, simply by choosing the right solvent conditions and solvent sequences. These MCMs can have spherical shapes, like hamburgers, clovers, or footballs, or they reversibly form worm-like structures with alternating compartments. The different compartments can be loaded with various nanoparticles or drugs.

In a systematic approach we combine particle geometries with internal morphology and thereby establish a library of so far unprecedented nanostructures. We designed the solvophilic block C to control the geometry of the nanostructure from spheres, cylinders to sheets and vesicles, while the two solvophobic blocks, A and B, are tailored to intrinsically phase-separate within the confined space of the nanostructure. Depending on the volume ratios of the two hydrophobic blocks, phase separation is observed inside the core according to morphologies as known from bulk, i.e. spherical, cylindrical, gyroidal and lamellar morphology.

A new triblock terpolymer, polybutadiene-block-poly(quaternized 2-vinylpyridene)-block- poly(methacrylic acid) (PVqMAA) forms multicompartment micelles in water with patches of an interpolyelectrolyte complex (IPEC) between the shorter cationic and a part of the longer anionic block. Interaction of the PMAA corona of these micelles with block copolymer of a polycation and poly(ethylene oxide) leads to complex core-shell-shell-corona micelles or even “paddle-wheel” structures. These structures are used host nanoparticles or drugs.

ML-09

NANOSTRUCTURED THERMOSETS FROM SELF-ASSEMBLING PROCESSES

J. F. Gérard[a], J. Duchet[a], S. Livi[a], F. Lortie[a], J. Bernard[a], L. Dai[b]

[a]*Ingénierie des Matériaux Polymères UMR CNRS 5223, Université de Lyon, INSA Lyon, F-69621 Villeurbanne, France*

[b]*Xiamen University, College of Materials, Xiamen, Fujian 361005, RPC*

(jean-francois.gerard@insa-lyon.fr)

Self-assembling processes could be combined with conventional thermoset polymer chemistries such as step polymerization encountered for epoxies or free radical polymerization for unsaturated polyesters or acrylates. In fact, innovative polymer materials which can display non conventional behaviors, *i.e* self-healing, stiffness-toughness combination, surface wettability, etc can be designed from such an approach. In fact, functionalities at nanoscale can be introduced from self-assembling of well-defined nanobuilding blocks of pre-formed nano-objects such as polyoligomeric silsesquioxanes (POSS) and organic or organic/inorganic block copolymers. Ionic liquids and supramolecular units could be also considered to design nanostructures leading to tailored physical behaviors of the resulting polymer networks.

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ML-10

SELF-ASSEMBLY OF SOFT MICROGELS IN BULK AND AT INTERFACES

W. Richtering

Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

We investigate the behavior of soft microgels in solution as well as at interfaces. In particular we study three different types of microgels: (i) core-shell microgels with a solid silica core surrounded by one or two shell cross-linked temperature sensitive polymers (with different cross-link densities); (ii) the corresponding hollow microgels where the core was dissolved; and (iii) ultra-low cross-linked PNIPAM microgels. The structure in solution was determined by means of light and neutron scattering employing contrast variation. The structure of the microgels at interfaces was investigated by scanning force and electron microscopy.

Compression isotherms of the microgel-laden oil-water interfaces were determined. They show that the removal of the core leads to an increase of the surface pressure at low compression and the same effect can be observed when the polymer crosslink density is decreased. Low cross-link density and a missing core thus facilitate spreading of the polymer chains at the interface and, at high compression, hinder the transition to close hexagonal packing. It is especially remarkable that a low cross-link density leads to a high compression modulus at low compression, while this behavior is reversed at high compression. This is related to an enhanced spreading of polymer chains at the interface and thus high adsorption energy. These conclusions are fully supported by computer simulations, which show that the cross-link density of the polymer shell defines the degree of deformation at the interface. Additionally, the core restricts the spreading of polymer chains at the interface. These results illustrate the special behavior of soft microgels at liquid interfaces.

Increasing the concentration of microgels at the interface via compression in a Langmuir trough leads to highly ordered 2D structures that can be transferred to a solid substrate. These can be used as templates for the preparation of vertically aligned nanowires.

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ML-11

SELF-ASSEMBLY OF PROTEINS AND POLYELECTROLYTES: COMPARING EXPERIMENTS TO THEORY AND SIMULATIONS

J. Dzubiella, M. Ballauff

Helmholtz-Zentrum Berlin and Institute of Physics, Humboldt University Berlin

Association of proteins with nanoparticles is a much-discussed problem in soft matter science and nanomedicine [1]. In all case charge-charge interactions play a major role. Proteins bear charges on their surface, often clustered into patches which will interact strongly with polyelectrolytes. In recent years we performed a series of systematic experimental and theoretical studies that include:

Interaction of linear polyelectrolytes with human serum albumin (HSA) in aqueous solution [2]. Here we could demonstrate that counterion release plays a major role for the process of binding. Moreover, the binding constant could be calculated in good approximation from simulations.

Adsorption of proteins to weakly charged microgels [3]. In particular, we developed a thermodynamic theory of protein adsorption onto these systems [4] and the competitive adsorption of proteins to these systems [5]. Given the parameters of single proteins, this theory predicts the competitive adsorption of an arbitrary number of proteins with semi-quantitative accuracy. Also, these parameters can be used to estimate the dynamics of protein adsorption [6].

Take-up of proteins by spherical polyelectrolyte brushes [7]. These particles consist of a solid core onto which long and highly charged polyelectrolytes are grafted. Previous work has shown that proteins are strongly adsorbed onto these particles [7,8]. Here too an advanced understanding of the driving forces for protein binding can be achieved by a combination of theory, simulations and experimental studies.

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ML-12

EFFECTS OF SPATIAL CONFINEMENT ON POLYMER STRUCTURE AND DYNAMICS*

Spiros H. Anastasiadis[a,b,#]

[a]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion Crete, Greece*
[b]*Department of Chemistry, University of Crete, Heraklion Crete, Greece*
(spiros@iesl.forth.gr, www.iesl.forth.gr)

We investigate the morphology and thermal properties of poly(ethylene oxide), PEO, in nanohybrids containing either layered silicates or silica nanoparticles. Mixing polymers with layered silicates can lead to intercalated hybrids when the interactions between the constituents are appropriate; these can serve as model systems for the investigation of the static and dynamic properties of macromolecules in nano-confinement of O(1nm). On the other hand, using silica particles of largely different sizes is an attempt to bridge the case of polymers confined within the galleries of layered silicates with that of polymer / single nanoparticle nanocomposites. Confinement is shown to modify the polymer structure, e.g., its crystallinity, with the effect being qualitatively different for different types of confinement. The behavior in systems containing different ratios of large-to-small silica nanoparticles is found intermediate between that of PEO/montmorillonite and that of PEO/silica with single-size particles. The behavior can be tuned by varying the ratio of large to small nanoparticles. The dynamics of the confined polymers is probed by dielectric spectroscopy and quasi-elastic neutron scattering. The very local dynamics of the confined chains show similarities with those in the bulk, whereas the segmental dynamics depend very strongly on the polymer/inorganic interactions varying from much faster to much slower or even frozen dynamics as the strength of the interactions increases.

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In collaboration with K. Chrissopoulou, H. Papananou, K. Androulaki, S. Bollas, S. Fotiadou, E. Perivolari, I. Tanis, K. Karatasos, B. Frick, K. Andrikopoulos, G. A. Voyiatzis, M. Labardi and D. Prevosto.

ORAL PRESENTATIONS

OP-01

USING SUPRAMOLECULAR HANDLES TO ORCHESTRATE POLYMER SELF-ASSEMBLY

G. M. ter Huurne, A. R. A. Palmans, E. W. Meijer, I. K. Voets

Laboratory of Macromolecular and Organic Chemistry & Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, P.O. Box 513, 5600 MB, the Netherlands

A beautiful illustration of hydrogen-bond driven assembly in solution is the supramolecular polymerization of C3-symmetrical discotics based on benzene-1,3,5-tricarboxamides (BTAs) into stiff, helical, one-dimensional 'stacks'. When these BTAs are coupled to a polymeric backbone, they force the chain to adopt a conformation far different from that without the grafted BTAs.[1-3] It is as if the graft copolymer folds via non-covalent interactions between pendant hydrogen-bonding motifs – analogous to proteins – into a compartmentalized structure: a single chain polymeric nanoparticle (SCPN). Small angle neutron scattering experiments on such water-soluble graft copolymers revealed that solvent- and temperature-induced stacking of the pendant supramolecular motifs forces SCNPs to adopt an elongated conformation.[2] Counterintuitively, the polymers adopt a more compact conformation at elevated temperatures when hydrogen bonds are largely broken.[1] In addition, spectroscopic experiments showed a lack of cooperativity in the folding behaviour, which is in strong contrast to the folding of globular proteins. These findings are intricately related to the balance between multiple driving forces, hydrogen bonding and hydrophobic interactions, which determines the architecture of the polymer as well as its colloidal stability. Understanding how macromolecular structure and physico-chemical factors determine the nature of SCPN folding is crucial to further their application potential as polymer-based catalysts, sensors, drug-delivery systems, and coatings.[4]

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OP-02

POLYPEPTOIDS AND POLYESTERS AS ALTERNATIVES TO METHACRYLIC SELF-ASSEMBLIES

J. Gaitzsch[a,b], K. Karu[b], G. Battaglia[b], W. Meier[a]

[a]*Department of Chemistry, University of Basel, Klingelbergstrasse 80,*
4056 Basel, Switzerland
[b]*Department of Chemistry, University College London, 20 Gordon St,*
London WC1H 0AH, United Kingdom
(jens.gaitzsch@unibas.ch)

Polymersomes are biomimetic vesicles of amphiphilic block-copolymers.[1] A major challenge towards their future development is to make them biodegradable by the means of defined polyamides (polypeptoids) and functional polyesters from radical ring-opening polymerisation.
We show the formation of vesicles from amphiphilic block-copolypeptoids, both as oligomers and as polymers. The peptoids, synthetic analogues to peptides, were mainly synthesised from solid phase synthesis and their their hydrophilic to hydrophobic aspect ratio was designed to favour vesicle formation. Using a range of hydrophilic parts, we analysed their influence on the quality of the actual peptoids generated but also how different hydrophilic part influence vesicle formation. We found peptoids to be quite resistant to swelling but were able to form peptoidosomes for all peptoids investigated.[2]

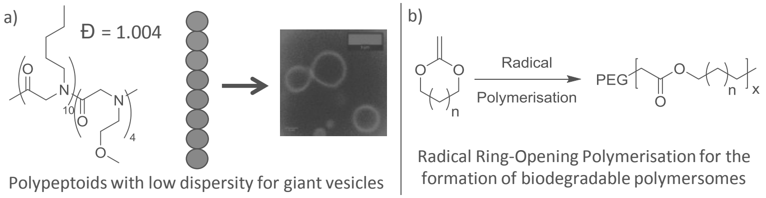

Figure 1: (a) Peptoids from solid phase synthesis and their self-assembly into giant vesicles. (b) Radical Ring-Opening Polymerisation for the formation of polyesters.

In very recent studies and ongoing research we show how well radical ring opening polymerisation[3] from cyclic ketene acetals to create biodegradable polyesters unavailable from other polymerisation techniques.

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OP-03

PROCESS-DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMER MATERIALS

M. Müller, W. H. Li, D. W. Sun, J. Tang, Q. Tang

Institute for Theoretical Physics, Georg-August University, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
(mmueller@theorie.physik.uni-goettingen.de)

The free-energy landscape of copolymer materials exhibits a multitude of metastable minima that correspond, e.g., to alternate periodic phases like hexagonally perforated lamellae, grain boundaries between domains of different orientations, or local defects. The barriers between these metastable states exceed the thermal energy scale by far and the thermodynamically stable morphology that corresponds to the absolute minimum often cannot be reached in experiments and simulations. Process-directed self-assembly refers to strategies that reproducibly direct the kinetics of self-assembly into a desired (meta)stable morphology by temporal control of thermodynamic variables, e.g., temperature, pressure. solvent contents, or interaction parameters. This strategy allows to access new morphologies, e.g., the bicontinous I-WP network morphology, that do not correspond to stable bulk phases or control the orientation of the microphase-separated domains. Using computer simulation we illustrate different processing protocols, e.g., pressure jumps,[1] solvent-annealing protocols,[2] roll-casting,[3] or spray coating, and demonstrate how the non-equilibrium, unstable initial condition dictates the spinodal kinetics of structure formation into a desired morphology. Since the initial kinetics occurs on the same time scale as the relaxation of the molecular conformations, chain conformations cannot be assumed to be in equilibrium with the instantaneous densities but additional order-parameters, e.g., the variance of the lowest Rouse-modes or the fraction of bridges in multiblock copolymers, are required to characterize the rapid structure evolution out of a non-equilibrium state into the nearest metastable morphology.

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OP-04

PROBING PROTEIN FOULING AND DNA COMPLEXATION WITH BIOCOMPATIBLE BLOCK COPOLYMERS

P. Štěpánek[a], E. Jäger[a], A. Jäger[a], F.C. Giacomelli[b]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*
[b]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09210-170 Santo André, Brazil. (stepanek@imc.cas.cz; www.imc.cas.cz)*

We have been studying the interaction of structurally different biocompatible block copolymer nanoparticles (NPs) after contact with complex biological media, as well as, for efficient DNA condensation (Fig. 1) by using several scattering techniques as, dynamic (DLS), static (SLS) and electrophoretic (ELS) light-scattering, fluorescent correlation spectroscopy (FCS), and isothermal titration calorimetry (ITC) and circular dichroism (CD) spectroscopy. Selective protein fouling on specific NPs was evidenced by using DLS/ELS measurements. In other NPs systems the protein adsorption event was dependent on the size, chain length, surface curvature, and hydrophilic chain density of the assemblies. Finally, through the use of FCS the DNA condensation ability of different environmentally responsive block catiomers was evaluated. The combination of the techniques shows that one of the catiomers efficiently condenses DNA with higher thermodynamic outputs than the other evalauted.

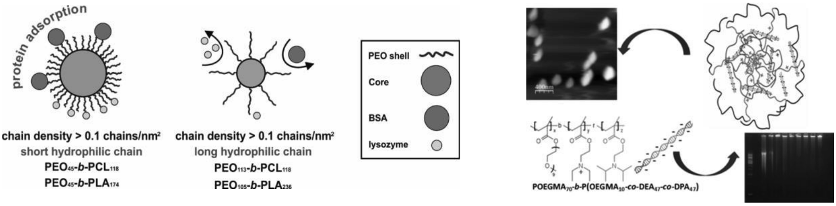

Figure 1. Size, chain length, surface curvature, and hydrophilic chain density effects on protein adsorption (*left*) and efficient DNA complexation from specific catiomer assemblies (*right*).

Financial support from Norwegian Grants (grant 7F14009), the Grant Agency of the Czech Republic (grant 16-02870S) and the Ministry of Education, Youth and sports (grant LH14292; grant POLYMAT LO1507) is gratefully appreciated.

OP-05

LIGHT- AND pH-RESPONSIVE POLYMERSOMES FOR SYNTHETIC BIOLOGY

D. Appelhans[a], B. Iyisan[a,b], H. Gumz[a,b], X. Liu[a,b], B. Voit[a,b]

[a]*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6,*
01069 Dresden, Germany
[b]*Technische Universität Dresden, 01062 Dresden, Germany*
(applhans@ipfdd.de, www.ipfdd.de)

Nano- and microobjects such as polymersomes, polymeric vesicles and hollow capsules are considered as artificial counterparts of natural liposomes. Those objects are suited materials for mimicking various cellular functions due to their high chemical and mechanical stability.[1,2] For their use in synthetic biology controlled membrane permeability or the controlled degradability of those objects are mandatory key characteristics to mimic biological processes or to use them as synthetic nanoreactors.

Here, we present our concept of pH-stable, pH-responsive and dual-responsive polymersomes in synthetic biology.[3,4] Examples are presented in respect to pH-switchable synthetic nanoreactors,[5] pH- and temperature-controlled diffusion processes[6] as well as controlled docking[4] and undocking processes inside and outside of polymersomes. Moreover, post-encapsulation of enzymes by polymersomes and post-conjugation processes of polymersomes surface[4] are further key tools to establish multicompartmentalized capsules in future work for synthetic biology.

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OP-06

SMART POLYMERSOMES: TUNABLE pH-SENSITIVITY AND ENZYME ENCAPSULATION

H. Gumz[a,b], V. Krönert[c], B. Voit[a,b], D. Appelhans[a]

[a] *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*

[b] *Organische Chemie der Polymere, Technische Universität Dresden und Center for Advancing Electronics Dresden, 01062 Dresden, Germany*

[c] *Hochschule für Technik und Wirtschaft, 01069 Dresden, Germany*

(gumz@ipfdd.de)

In recent years, large efforts were made to develop smart polymeric systems feasible for applications in drug delivery and synthetic biology. Polymersomes, artificial analogues of liposomes prepared by the self-assembly of amphiphilic block copolymers are promising candidates for such purposes. The resulting bilayer membranes of polymersomes are thicker compared to liposomes resulting in mechanically and chemically much tougher vesicles.[1] Combining the incorporation of pH-responsive and photo crosslinkable units into the block copolymers used for assembly of the polymersomes leads to reversible swelling and shrinking behaviour of polymersomes´ membrane upon changes of the pH.[2]

In order to adapt polymersomes for various applications a threefold approach was developed. At first, the exact pH value at which vesicle swelling or shrinking occurs could be precisely and continuously adjusted by means of the block copolymer synthesis and composition. Secondly, the hydrolytically active enzyme Esterase has been encapsulated within the polymersomes resulting in nanoreactors whose activity can be switched on and off in respect to the pH. Even at acidic conditions while the vesicle membrane is permeable for the substrate no leakage of enzyme could be detected over a time of 48 hours. Thirdly, the polymersome corona was decorated with functional groups allowing for strong and highly specific non-covalent conjugations[3] such as Biotin-Avidin-interactions enabling conjugation of the polymersomes to proteins or other biological entities.

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OP-07

SELF-ASSEMBLY OF SUGAR-BASED BLOCK COPOLYMERS BY SOLVENT VAPOR ANNEALING

Y. Liao, R. Borsali*

Centre de Recherches sur les Macromolécules Végétales (CERMAV, UPR-CNRS 5301) and Grenoble Alpes University, 38041, Grenoble Cedex 9, France

(borsali@ceramv.cnrs.fr, www.cermav.cnrs.fr/en)

Block copolymers (BCP) have attracted considerable research attention and industrial development due to their capability of forming long range ordered patterns at the nanometer scale. Hydrophilicity-hydrophobicity imbalance could result in high incompatibility between saccharides and synthetic polymers, which is exploited by our group to study natural-synthetic hybrid BCPs with a high χ parameter. The natural-synthetic hybrid BCP polystyrene-block-maltoheptaose (PS-b-MH) used in this study is synthesized by linking end-functionalized blocks via click chemistry [1]. The PS-b-MH can self-assembled into hexagonally close-packed cylinder patterns with sub-10 nm feature size [2], which exhibits for example high performance in nonvolatile transistors memory applications [3, 4]. To scale up the production and improve the purity of the product, homogenous catalysis CuBr used in previous synthesis is replace by a heterogeneous catalysis copper nanoparticles. Here we report that the PS-b-MH could self-assemble into different nanostructures including horizontal cylinders, vertical cylinders and body-centered cubic structures by changing the parameter of solvent vapor annealing. The phase transitions of the PS-b-MH in the solvent vapor annealing are investigated systematically.

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OP-08

SELF-ORGANIZATION OF POLYMERIC NANO-COMPARTMENTS OR NANO-REACTOR-ORIGAMI

J. Liu[a], V. Postupalenko[a], S. Lörcher[a], D. Wu[a], M. Chami[b], W. Meier[a],
C. G. Palivan[a]

[a]*Department of Chemistry, University of Basel, Klingelbergstrasse 80,
Basel 4056, Switzerland*

[b]*Centre for Cellular Imaging and Nano Analytics, Biozentrum, University
of Basel, Mattenstrasse 26, 4058 Basel, Switzerland*

samuel.loercher@unibas.ch

Polymeric nano-reactors are composed of a self-assembled polymeric membrane, an encapsulated catalytic entity and a component enabling molecular transport across the membrane. By controlled clustering of such nano-reactors molecular systems can be engineered. We report a simple way to cluster polymeric nano-reactors, assembled from PMOXA-PDMS-PMOXA in aqueous conditions, to yield distinct geometrical configurations of polymeric vesicles as depicted in figure 1. Furthermore, the distance between the respective reactors can be fine tuned in the order of 1 nm.

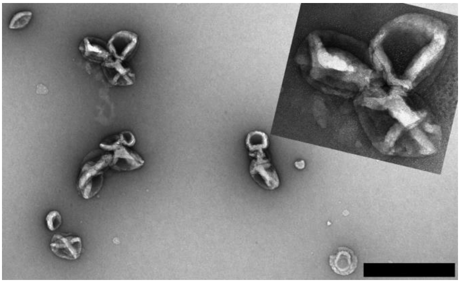

Figure 1. TEM overview of nano-reactor-origami, scalebar is 1000 nm, the inset a magnification of the top left cluster.

OP-09

NOVEL TRIPHILIC BLOCK COPOLYMERS BASED ON POLY(2-METHYL-2-OXAZOLINE)-*BLOCK*-POLY(2-OCTYL-2-OXAZOLINE) WITH DIFFERENT TERMINAL PERFLUOROALKYL FRAGMENTS

S. Filippov[a], L. Kaberov [a], B. Verbraeken[b], M. Hruby[a], L. Kovacik[c],
A. Riabtseva[a], P. Stepanek[a], R. Hoogenboom[b]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*

[b]*Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4, B-9000 Ghent, Belgium*

[c]*Institute of Cellular Biology and Pathology, First Faculty of Medicine, Charles University, Albertov 4, 128 01, Praha 2, Czech Republic*

We report the synthesis and solution properties of novel fluoro-containing copolymers. Our synthetic approach provides an easy way to attach a C_nF_{n2+1} fluorinated block to poly(2-MeOx)-*block*-poly(2-OcOx) diblock copolymer and combine hydrophilic, hydrophobic and fluorophilic moieties together. Triblock copolymers were different in the length of the florinated block. By a variety of experimental methods such as DLS, and cryo-TEM it was proven that all synthesized copolymers self-assembly in nanostructures in aqueous milieu. The structure and shape of nanostructures is controlled by the ratio between blocks. The presence of single layer, multi-layer polymersomes and worm-like micelles were visualized in aqueous solutions (Figure 1).

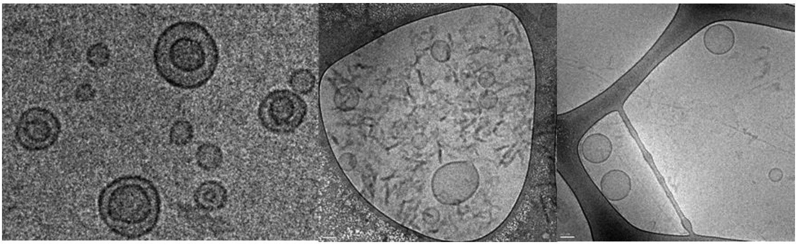

Figure 1. Cryo-TEM micrographs of 1 wt.% aqueous solutions of diblock $MeOx_{30}$-$OcOx_{20}$ (left), triblock $MeOx_{30}$-$OcOx_{20}$-C_8F_{17} (middle), and triblock $MeOx_{30}$-$OcOx_{20}$-$C_{12}F_{25}$ (right) copolymers.

OP-10

HIGHLY ORDERED NANOPOROUS FILMS FROM SUPRAMOLECULAR DIBLOCK COPOLYMERS WITH H-BONDING JUNCTIONS

D. Montarnal[a], N. Delbosc[a], C. Chamignon[a], M.-A. Virolleaud[a], Y. Luo[b], C. J. Hawker[b], E. Drockenmuller[a], J. Bernard*[a]

[a]IMP, INSA-Lyon, 17 av Jean Capelle 69621 Villeurbanne, France

[b]Materials Research Laboratory, University of Santa Barbara, USA

Herein, we report on the design of H-bonding precursors that combine complementary associative groups with exceptional binding affinities and thiocarbonylthio moieties enabling RAFT polymerization. Well defined PS and PMMA supramolecular polymers with molecular weights up to 30 kg. mol^{-1} are synthesized and shown to form highly stable supramolecular diblock copolymers (BCPs) when mixed, in non-polar solvents or in the bulk. Hierarchical self-assembly of such supramolecular BCPs by thermal annealing affords morphologies with excellent lateral order, comparable to features expected from covalent BCP analogues. Washing of the resulting materials with protic solvents affords nanoporous materials without resorting to crosslinking or invasive chemical degradations (Figure 1).[1]

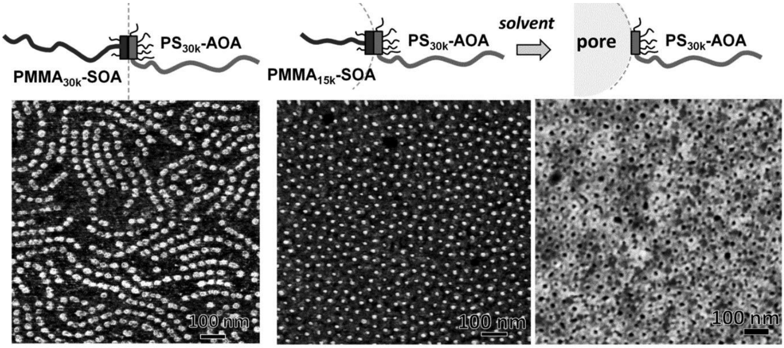

Figure 1. Left and middle: AFM phase images of **PS$_{30k}$-*supra*-PMMA$_{30k}$** and **PS$_{30k}$-*supra*-PMMA$_{15k}$** thin films, Right: AFM height image of **PS$_{30k}$-*supra*-PMMA$_{15k}$** after washing. Top: General sketch of the packing at the interface.

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OP-11

ENCAPSULATION OF SMALL MOLECULES BY POLY(ETHYLENE GLYCOL)-GRAFT-POLY(VINYL ACETATE) UNIMER MICELLES

A. Bartolini[a], P. Tempesti[a], C. Resta[a], D. Berti[a], J. Smets[b], Y. G. Aouad[c], P. Baglioni[a,*]

[a]*Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, via della Lastruccia 3, Sesto Fiorentino (FI), 50019, Italy*
[b]*Procter & Gamble, Temseelan 100, 1853 Strombeek Bever, Belgium*
[c]*Procter & Gamble, Winton Hill Technical Center, 6100 Center Hill, Cincinnati, OH 45224*
**bartolini@csgi.unifi.it*

Single chain nanoparticles are unimolecular nano-objects typically obtained by the self-folding of linear polymer chains that possess small pendant groups or longer side chain that can interact with each other via intra-chain interactions.[1] From an industrial point of view a concentration of particles higher than the typical 1 mg mL^{-1} is recommended.[2]

In this work we report on the formation of unimer micelles composed of amphiphilic poly(ethylene oxide)-*graft*-poly(vinyl acetate) copolymers that undergo self-folding in water driven by hydrophobic interactions only. This results in the formation of unimer micelles with a hydrodynamic diameter of about 20 nm. This material is best suitable for technical applications because of the simple molecular architecture and stability of unimeric micelle suspensions up to 100 mg mL^{-1}. The so-obtained single-chain globular particles are able to swell upon loading with small hydrophobic molecules therefore promoting micellar solubilization of flavors or drugs, which could be of interest in the food and pharmaceutical industry.

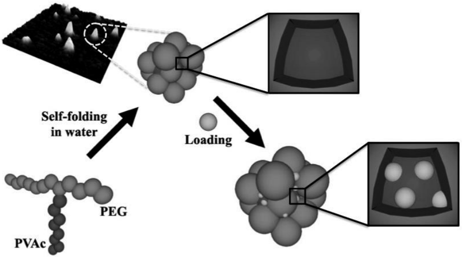

Figure 1

Schematic representation of PEG-g-PVAc chains self-folding into unimer micelles and swelling upon loading of small hydrophobic molecules.

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OP-12

POLYMER MEMBRANES DECORATED WITH PROTEINS: SMART SELF-ASSEMBLED FUNCTIONAL NANOSYSTEMS

Cornelia G. Palivan

Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

New concepts that combine multifunctional compounds with stable, safe carriers or membranes are on focus in a variety of domains, such as medicine, catalysis, environmental science, food science and technology.[1] In this respect, suitable amphiphilic block copolymers are ideal candidates for applications because they can self-assemble into 3D supramolecular assemblies, such as compartments, or planar membranes. Such synthetic flexible membranes have a superior stability, and robustness compared to the lipid based membranes, and can be obtained with a variety of physical and chemical properties. The properties of such membranes can be extensively controlled via chemical composition, molecular weight and the hydrophilic-to-hydrophobic block length ratio of the polymers.[2] An elegant manner to implement smart behavior of polymer membranes is to insert biopores, which possess an intrinsic responsive property. By combining these polymeric membranes with suitable biological entities, e.g., by incorporating integral membrane proteins or by enzyme encapsulation in polymer compartments it is possible to provide well-defined functions, such as molecular recognition, cooperation, and catalytic activity.[1]

Here, we present distinct spaces for desired reactions at the nanometer scale based on protein-polymer assemblies as compartments with triggered activity or as bilayers on solid support.[3,4] Biopores/channel proteins inserted into the polymer membrane selectively control the exchange of substrates and products with the environment of compartments, resulting in development of stimuli-responsive compartments, which preserve their architecture, while allowing specific *in situ* reactions. Channel proteins/biopores inserted in solid supported membranes serve for a controlled transport of ions or molecules through the synthetic membrane. Protein-decorated synthetic membranes represent smart hybrid systems, which open new avenues in various domains, as for example protein therapy or biosensing approaches.

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OP-13

SELF-ASSEMBLED STRUCTURES OF POLYMERS FOR MEDICAL APPLICATIONS

B. Nyström

Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo, Norway

**bo.nystrom@kjemi.uio.no*

In the first part of the presentation some special features of poly(N-isopropylacrylamide) (PNIPAAM) in solution will be discussed. It will be shown that the value of the cloud point drops with increasing molecular weight of PNIPAAM and increasing polymer concentration[1].

Small angle X-ray scattering experiments on triblock copolymers, composed of MPEG-PNIPAAM-charged block with a PNIPAAM block of various lengths; reveal some interesting temperature–induced structural changes as result of the self-assembling process. For triblock copolymers with a short PNIPAAM block no self-assembling is observed. The copolymers with medium and long PNIPAAM block length self-assemble and the structure of the micelles varies with the PNIPAAM block length. The polymer with medium PNIPAAM block length forms spherical micelles, whereas the polymer with a long PNIPAAM block length forms cylindrical micelles[2].

Hyperbranched polymers and dendrimers have attracted a great deal of interest as nanocarriers due to their well-defined structures and high density of surface groups[3]. Structure, internal density distribution, and size of hyperbranched poly(ethylene imine) (PEI) functionalized with various amounts of maltose (PEI-Mal) in phosphate buffer were studied by small angle X-ray scattering (SAXS). SAXS results revealed a broad segmental radial density distribution, i.e. a "fluffy" globular structure rather than a distinct core-shell structure with a high-density compact core and a low-density corona. This suggests that the maltose units are rather evenly distributed both in the interior and on the surface of the species with a PEI-core. In contrast to the core-shell model expected from the synthesis of the PEI-Mal architectures[4], the SAXS results reveal that this is not a realistic model.

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OP-14

COMPUTER MODELING OF DIBLOCK COPOLYMER SELF-ASSEMBLY IN SOLUTION: FROM DYNAMICS TO HYDRATION

E. E. Dormidontova

Polymer Program, Institute of Materials Science and Physics Department,
University of Connecticut, 97 North Eagleville Road,
Storrs, CT 06269, USA

Diblock copolymer self-assembly has been actively studied over the last two decades with considerable progress made in understanding principles of equilibrium self-assembly. With the development of high-resolution experimental techniques and technological advancement in computational power, now it become possible to look more closely into the important features of self-organization, which have not been accessible until now. Based on the results of computer simulations, we'll discuss two examples of such features: dynamics of diblock copolymer assembly solution and hydration in the corona-forming polymer of spherical micelles. Polymer self-assembly and chain exchange between micelles in solution have been studied by dissipative particle dynamics, while to obtain insights into polymer corona hydration we applied a combination of coarse grained and atomistic molecular dynamics simulations. We analyzed the effect of polymer length and diblock copolymer composition on the dynamics of self-assembly and corona hydration in micelles. Both of these features are important for practical applications of self-assembled nanostructures, e.g. in nanomedicine, as they affect micelle stability, drug delivery and anti-fouling properties. In general these elements are also of fundamental importance for understanding the kinetic pathways of self-assembly, solvent distribution inside micelles and solvent-related effects affecting equilibrium micelle structure.

OP-15

COMPUTER STUDY OF THE ELECTROSTATIC CO-ASSEMBLY IN NON-STOICHIOMETRIC MIXTURES OF BLOCK POLYELECTROLYTES

K. Procházka[a], K. Šindelka[a], Z. Limpouchová[a], M. Lísal[b]

[a]*Department of Physical and Macromolecular Chemistry, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic*

[b]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135/1, 165 02, Prague 6, Czech Republic*

kar.prochaz@centrum.cz

In this communication, we present new simulation results concerning the electrostatic assembly in non-stoichiometric mixtures of two double-hydrophilic copolymers composed of one neutral water-soluble block and one (either positively or negatively charged polyelectrolyte block). The study confirms basic conclusions on the behavior published by van der Burgh et al. [1], but it simultaneously reveals new features and shows that the behavior is more complex than expected.

Dissipative particle dynamics (DPD) is a versatile coarse-grained simulation technique which (in its original variant) employs three types of forces: (i) soft coarse-grained repulsion, (ii) dissipative force (emulating friction) and (iii) random fluctuating force (emulating thermal collisions). It enables studies of complex polymer systems and it has been used also for successful simulations of polymer self-assembly. Although the electrostatic interactions have been included into DPD by Groot [2] some time ago, most authors still use the so called "ion-free" approach [3], when studying the self-assembly of polyelectrolytes (PE). In this variant, the electrostatic interactions are ignored at all and the soft repulsion between coarse-grained beads is described by effective pH-dependent or ionic strength-dependent parameters, which are recalculated from various dependences of macroscopic properties of the system on pH and ionic strength.

In contrast to the "ion-free" approach, we use DPD variant which includes explicit description of electrostatic forces between smeared charges localized on PE chains and on counterions for studies of self-assembling PE systems. [4,5] The simulations are computationally demanding and significantly slower than standard DPD runs, but we believe that the explicit electrostatics should be always used in DPD studies of systems with electric charges. The empowered model takes the entropy of counterions and electrostatic correlation effects directly into account (at least at the coarse-grained level of Kuhn segments) and enables detailed study aimed at the elucidation of principles of the behavior.

Acknowledgements: Czech Science Foundation, grant GA ČR: P106-12-0143.

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OP-16

COUPLING OF IONIZATION AND CONFORMATION IN pH-RESPONSIVE POLYELECTROLYTES

P. Košovan[a], L. Nová[a], F. Uhlík[a], E. B. Zhulina[b,d], O. Borisov[c,d],
F. A. M. Leermakers[e]

[a]*Dept. of Phys. and Macromol. Chemistry, Charles University in Prague, Czech Republic*
[b]*Inst. of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia*
[c]*University of Pau, France*
[d]*St. Petersburg National University of Information Technologies. Mechanics and Optics, St. Petersburg, Russia*
[e]*Wageningen University, The Netherlands*
peter.kosovan@natur.cuni.cz

The ionization behaviour of pH-responsive (weak) polyelectrolytes is strikingly different from their monomeric counterparts. By means of molecular simulations we unravel intricate features of ionization of linear and branched polyelectrolytes and relate them to the conformational changes. First we demonstrate the principles on hydrophilic linear and star-like polyelectrolytes. Then we focus on hydrophobic star-like polyelectrolytes, which exhibit intra-molecular self-organization rather than macroscopic phase separation, because of the interplay of short-range hydrophobic attraction and long-range electrostatic repulsion. We unravel how the morphology of the intra-molecular nanostructures can be controlled through the topology of the macromolecule and by adjustable ionization. While both weak and strong polyelectrolyts are collapsed when uncharged, and expand to full stretching of arms at high ionization, they exhibit quite different intermediate scenarios. The strong ones self-organize to bundles of arms, while the weak ones form intra-molecular micelle-like structure. Here intramolecular disproportionation leaves some arms in a collapsed virtually neutral core, while others are substantially ionized and stretched in the corona.

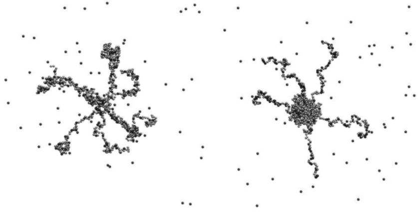

Figure 1.
Simulation snapshots of the strong and weak (pH-responsive) polyelectrolyte star under marginally poor solvent conditions and similar degree of ionization.

OP-17

PREDICTION OF POLYMERIC SELF-ASSEMBLY BY SELF-CONSISTENT FIELD COMPUTATIONS

R. Tuinier[a,b]

[a]*Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands*
[b]*Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Utrecht*

An overview of work is presented on polymer (self- and co-)assembly to make particles. The self- and co-assembly of block copolymers in selective solvents is a well-known approach for generating a wide range of submicron scale morphologies, including spherical micelles, wormlike micelles, or vesicles. These can be exploited in for instance drug delivery, encapsulation, and cosmetics. First I will give a brief introduction into the numerical self-consistent field (SCF) lattice method we use to predict various properties of such assembled structures. Subsequently, a few examples are given of work where SCF has been used and compared to experiment. First triblock copolymer particles are considered made via a precipitation method[1]. It is shown that SCF can be employed to accurately predict the size of self-assembled triblock copolymer micelles. These systems can be used to encapsulate hydrophobic compounds into aqueous systems. In order to encapsulate hydrophilic molecules such as proteins vesicles are interesting vehicles. Polymerization-induced assembly (PISA) can nowadays be used to synthesize vesicles up to high concentrations. However, this leads to rather polydisperse vesicles, which is undesired. Using SCF we predicted that combining a vesicle forming diblock copolymer plus a spherical micelle forming diblock copolymer leads to very monodisperse vesicles. This was experimentally confirmed[2]. Finally, it will be shown how SCF was used to predict the preferred self-assembled morphology of charged diblock copolymers composed of methacrylic acid (MAA) and methyl methacrylate (MMA) blocks in aqueous salt solutions[3]. PMMA-PMAA polymers are interesting candidates for replacing surfactants in emulsion polymerization methods. Emulsion polymerization is one of the most widely used industrial process for making waterborne polymers. A disadvantage is the use of surfactants in emulsion polymerization: these have a negative influence on adhesion and water sensitivity of coatings. Amphiphilic block copolymers might be better alternatives. It is shown how SCF correctly predicts the experimentally determined morphologies made from well-defined PMMA-PMAA polymers.

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OP-18

COMPLEXES OF CATIONIC POLYMERS WITH ANIONIC LIPOSOMES

A. A. Yaroslavov

Chemistry Department, M.V. Lomonosov Moscow State University,
Leninskie Gory 1-3, Moscow, 119991, Russian Federation

(yaroslav@genebee.msu.ru)

Composition and properties of complexes are discussed, formed by cationic polymers with different architectures and small unilameller vesicles, 40-60 nm in diameter, composed of an anionic lipid, e.g. diphosphatidylglycerol (cardiolipin, CL^{2-}), and a zwitter-ionic lipid, e.g. egg yolk lecithin (EL).

Complexation of anionic vecilsles (liposomes) with liner polycations can be accompanied by structural re-arrangements in the liposomal membranes: lateral lipid segregation, highly accelerated transmembrane migration of lipid molecules, incorporation of adsorbed polymers into the liposomal membrane, etc., and morphological changes in liposomes: their aggregation, fusion and disruption. Electrostatically adsorbed polycations can be completely removed from the membrane surface in water-salt solutions or in the presence of an anionic polymer. The above mentioned phenomena have been examined depending on the polymer composition, content of charged lipids, vesicle phase state and size; as well as ionic strength of solution. The observations we have made might be useful to interpret biological effects of polyelectrolytes and multicharged polymeric constructs. Evidence is provided for electrostatic adsorption of anionic liposomes onto the surface of 100-nm polystyrene particles bearing grafted linear cationic macromolecules (“spherical polycationic brushes”). The size, shape, and encapsulation ability of liposomes remain unchanged upon adsorption onto the brushes. By using a mixture of liposomes with variety of encapsulated substances, multi-liposomal complexes can be prepared with a high loading capacity and a controlled ratio of the contents. The supramolecular aggregates, representing an assembly of self-assemblies, have potential applications in the drug delivery field.

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OP-19

SELF-ASSEMBLING BIOHYBRID MATERIALS

C. Nardin

Université de Pau et des Pays de l'Adour - Equipe Physique Chimie des Polymères - 2 av. du Président Angot, 64053 Pau (France)
(corinne.nardin@univ-pau.fr)

The synergetic combination of synthetic and natural materials is an exciting topic of research since, on one hand, the theories and methods developed in polymer science might enable the establishment of the mechanisms of structure formation and modes of interaction of biological polymers and macromolecular self-assemblies thereof. On the other hand, the biological soft matter is a source of inspiration to develop materials of academic interests and of high potential for various applications in particular in biology and medicine.

DNA-copolymer self-assembly and the formation of interpolyelectrolyte complexes between nucleic acids and proteins are two examples which illustrate this duality. Self-assembling DNA-copolymers, which are composed of a nucleic acid sequence coupled to a hydrophobic polymer, do self-assemble in dilute aqueous solution and undergo crystallization in thin films like their fully synthetic counterpart. Of higher interest though is that these hybrids do assemble into functional structures, i. e. the nucleic acids engaged in self-assembly retain their capacity of hybridization or of specific recognition. These hybrids are especially designed to develop vectors for either sustained, targeted drug delivery or for gene therapy. Fine tuning of the DNA-copolymer composition to enhance intra-molecular interactions between nucleic acid grafts and the synthetic polymer backbone of a graft/comb DNA-copolymer of suitable composition enabled mimicking the nucleation polymerization into fibrillar structures according to which amyloid proteins self-assemble. These proteins have been identified in several neurodegenerative diseases. Prevent or disrupt their pathogenic macromolecular assembly is the current approach to identify a potential future cure. However, although the analogy between nucleic acids or polypeptides and charged polymers is obvious, few reports in the literature address the formation of interpolyelectrolyte complexes between nucleotide and peptide sequences to prevent or disrupt the macromolecular assembly of amyloids. Interpolyelectrolyte complex formation is an established mechanism in polymer science, which we are exploring to counterbalance the pathogenic association of amyloid proteins.

OP-20

EFFECT OF LYSOZYME COMPLEXATION ON THE THERMORESPONSIVE BEHAVIOR OF PnBA-b-PNIPAM-COOH MICELLAR AGGREGATES

A. Papagiannopoulos[a], A. Meristoudi[a], S. Pispas[a], U. Keiderling[b]

[a]*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 11635 Athens, Greece*

[b]*Helmholtz Zentrum Berlin, D-14109 Berlin, Germany*

(pispas@eie.gr, www.eie.gr)

Protein interactions with macromolecular nanostructures have been investigated intensely during the last two decades because of the high potential for application in protein separation, drug delivery, food science and tissue engineering[1]. Small angle scattering methods and analysis advancements has pushed the field forward by characterizing in detail the morphology of protein binding nanoparticles[2]. PNIPAM-containing polymers are under extensive study[3] due to the volume phase transition of PNIPAM in water at physiological relevant temperature which makes it a highly desirable component for stimuli responsive nanocarriers, in tissue engineering and biosensors and in the general field of smart materials.

We investigate the temperature-responsive morphology of PnBA-b-PNIPAM-COOH self-assembled hierarchical aggregates and the effect of interaction with lysozyme. A detailed small angle scattering analysis of the sensitivity of temperature response on polymer concentration demonstrates how complexation of lysozyme enhances the transition to aggregated interacting hard-core micelles at low concentrations. The scattering profiles are consistent with lysozyme accumulating in the vicinity of the micellar cores a finding that is supported by measurements in lysozyme contrast matched solvent. This study aims to extend the detailed small angle scattering morphological analysis of nanoparticle protein complexes and thermoresponsive self-assembled structures to protein loaded thermoresponsive nanostructures.

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OP-21

SEVEN YEARS OF RADIONUCLIDE LABORATORY AT THE INSTITUTE OF MACROMOLECULAR CHEMISTRY AS CR – IMPORTANT ACHIEVEMENTS

M. Hrubý, J. Kučka, J. Pánek, P. Štěpánek

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(mhruby@centrum.cz, www.imc.cas.cz)

For many important research topics in polymer science the use of radionuclides brings significant benefits concerning nanotechnology, polymer drug delivery systems, tissue engineering etc. This contribution describes important achievements of the radionuclide laboratory at the Institute of Macromolecular Chemistry AS CR in the area of polymers for biomedical applications. Particular emphasis will be given to water-soluble polymer carriers of radionuclides, thermoresponsive polymer radionuclide carriers, thermoresponsive polymers for local brachytherapy, polymer scaffolds modified with radiolabeled peptides and polymer copper chelators for the therapy of Wilson´s disease.

Financial support from the Czech Grant Foundation (grants # 13-08336S, 16-03156S and 16-02870S) and from the Ministry of Health of the Czech Republic (grants # 15-25781A and 16-30544A) is gratefully acknowledged.

OP-22

TOWARDS STIMULI RESPONSIVE ARTIFICIAL CELL ORGANELLES BY BIOMIMETIC ENGINEERING OF COMPLEX MEMBRANE PROCESSES

T. Einfalt[a], C. Edlinger[a], R. Goers[a,b], A. Najer[a], M. Spulber[a], C. G. Palivan[a]

[a]Department of Chemistry, University of Basel, Basel, Switzerland
[b]Department of Biosystems Science and Engineering, ETH Zürich, Basel, Switzerland (Tomaz.einfalt@unibas.ch)

Recent advances in engineering robust polymeric compartment spaces with catalytic activity have led to the development of the first polymersome based artificial cell organelle.[1] Systems more comparable to biological cell membranes should ideally present triggered activity *in vivo*, whilst preserving the nanocompartment architecture of the system.[2] We present here PMOXA-b-PDMS-b-PMOXA based polymersomes, whose synthetic membranes are equipped with chemically modified channel proteins, so that they are stimuli responsive. Outer membrane protein F, previously used for the development of the first artificial peroxisome, was chemically modified with a stimuli responsive molecular cap in order to serve as a reduction responsive molecular "gate". Upon successful cellular uptake these biomimetically engineered polymersomes can act on demand *in vivo* and present the next generation of stimuli responsive artificial organelles.

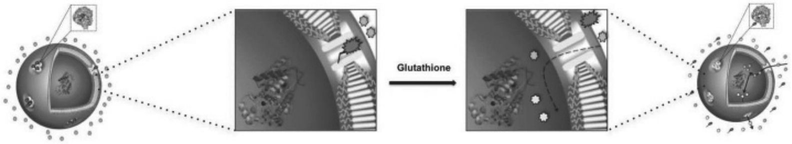

Figure 1. Representation of polymersome equipped with biomimetically engineered redox responsive protein gates.

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OP-23

CO$_2$-STIMULATED SHAPE AND MORPHOLOGICAL TRANSITIONS OF BLOCK COPOLYMER ASSEMBLIES

Q. Yan, Y. Zhao

Département de Chimie, Université de Sherbrooke Sherbrooke, Quebec, J1K 2R1, Canada

(Yue.zhao@usherbrooke.ca)

We report our studies on block copolymers (BCPs) whose self-assembled nano- or microstructures in aqueous solution can undergo a variety of shape and morphological transitions stimulated by CO$_2$. By introducing into BCP structures proper functionalities that can be protonated by the presence of CO$_2$, such as amidine, tertiary amine and benzimidazole, various types of covalent and supramolecular CO$_2$-responsive BCPs were designed and synthesized. We explored the use of CO$_2$ as a model physiological stimulus to induce and control the changes of BCP assemblies for bio-mimicking, including a sequence of transitions from microtubules to submicroscopic vesicles to nanosized micelles, diversiform deformations driven by a restricted hydration effect, and reversible dissociation/association.

OP-24

SELF-ASSEMBLY OF POLY(2-ALKYL-2-OXAZOLINE)S IN AQUEOUS SOLUTIONS

Z. Altıntaş[a], M. Amiriafshar[b], E. Beruhil Adatoz[c], P. Tatar Güner[a], A. Miko[a], A. L. Demirel[a,b,c]

[a]Chemistry Department, [b]Material Science & Engineering Program,
[c]Biomedical Science & Engineering Program,

Koç University, Istanbul, Turkey

(ldemirel@ku.edu.tr, home.ku.edu.tr/~sppc/)

The physicochemical properties of poly(2-alkyl-2-oxazoline)s (PAOX) depend on the alkyl side chain length. As the alkyl side chain length decreases, LCST of aqueous solutions increases, glass transition temperature (T_g) increases and bulk crystallization is significantly hindered. Among PAOX having shorter side chains, poly(2-ethyl-2-oxazoline) (PEOX) is the only member whose bulk crystallization was previously not reported. We have shown that self-assembled crystalline PEOX fibers form when aqueous PEOX solutions are kept above the cloud point temperature (T_c) for long times (days to weeks). The self-assembly into water insoluble fibers above T_c, a slow crystallization process, was enhanced by the addition of various sodium salts. The specific anion effects on T_c of aqueous PEOX solutions will be presented and the contribution of different mechanisms to phase separation at T_c and self-assembly will be discussed.

Small monocarboxylic acids form H-bonds in acidic solutions with PEOX. H-bonded complexation of acetic acid with PEOX in acidic aqueous solutions above T_c was found to enhance the self-assembly of PEOX into nanofibers. We investigated the potential of various carboxylic acids to form well-defined PEOX fibers in aqueous solutions as a function of pH, temperature, ionic strength and acid concentration. In order to understand the effect of polymer chemical structure, poly(N-isopropyl acrylamide) (PNIPAM) was also investigated and the results were compared. Possible mechanisms of H-bonded self-assembly will be discussed.

OP-25

HYDROPHILIC POLYMER BRUSHES SPONTANEOUSLY FORMED AS SEGREGATED FROM SILICONE MATRIX AT THE INTERFACE WITH WATER

T. Røn[a], I. Javakhishvili[b], S. Hvilsted[b], K. Jankova[b], S. Lee[a]

[a]*Department of Mechanical Engineering, Technical University of Denmark, Kgs. Lyngby, DK-2800, Denmark*

[b]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, DK-2800*

In this study, we present a new and simple way to form hydrophilic polymer brush chains as segregated from PDMS matrix at the interface with water surfaces and its technical and biomedical applications focusing on its unique slipperiness and antifouling properties in aqueous environment.[1] In this approach, termed as “inverted grafting-to approach”, hydrophilic polymer chains of amphiphilic diblock copolymers, such as PDMS-*b*-PAA or PDMS-*b*-PEG, dispersed within a silicone (PDMS) network are selectively segregated upon exposure to water and form dense, brush-like hydrophilic polymer chain layers of PAA or PEG. This approach can be applied to any materials on which PDMS film can be coated, such as elastomers, ceramics or metallic surfaces. An outstanding merit of the presently demonstrated approach is its excellent stability arising from selective solubility of PAA or PEG chains from the amphiphilic block copolymers and possible replenishment from internal sources when the initially formed polymer chains are damaged. In principle, this approach can replace other existing popular approaches to prepare polymer chain layers, such as “grafting-from” or “grafting-to” approaches in any applications. Considering its unique and excellent stability, we propose that applications under harsher environment or where long-term stability is required, such as tribological contacts, marine applications, or bio-implants are most appropriate. A few examples of aqueous lubrication revealing long-term lubricating effect and anti-fouling properties in marine or biomedical applications are presented along with structural characterization of the polymer brush layers.

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OP-26

PROMISING TAILOR MADE HOLLOW CHITOSAN / POLY(ACRYLIC ACID) NANOPARTICLES FOR ANTIBIOTIC THERAPY

S. Belbekhouche, O. Mansour, B. Carbonnier

Université Paris Est, ICMPE (UMR7182), CNRS, UPEC, F-94320 Thiais, France

(sabrina.belbekhouche@icmpe.cnrs.fr)

Recent progress in supramolecular chemistry leads to unparalleled control over the composition and shape factor of colloidal systems. Among them, the design of hollow capsules is a new expanding area of physical-chemical research.[1] Here, we report on the development of tailor made polymer capsules for potential applications in antibiotic therapy. Hollow nanospheres based on chitosan/poly (acrylic acid) (PAA) loaded with amoxicillin (a betalactam antibiotic) were elaborated via the layer-by-layer technique using gold nanoparticles as templates (strategy illustrated in Figure 1). The strategy consists on capsules elaboration through the sequential deposition of chitosan and poly(acrylic acid). Size, dispersity and concentration of the nanocapsules are easily fixed by the initial nanoparticle template, while wall thickness is dependent on the number of players. Capsules containing crosslinked chitosan were also prepared for the direct control of the drug entrapment/loading as small drug molecules containing amine groups (i.e. amoxicillin) can go across the chitosan/PAA layer and complex with the PAA.[2] The drug-loading content was up to 5%

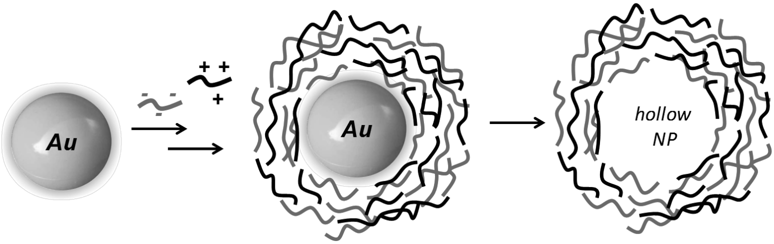

Figure 1. Schematic illustration of hollow nanocapsule elaboration by the polyelectrolyte layer by layer self-assembly strategy. (NP: nanoparticle)

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OP-27

SUPRAMOLECULAR SELF-ASSEMBLY OF DOUBLE HYDROPHILIC BLOCK COPOLYMERS AND THEIR USE AS STRUCTURE-DIRECTING AGENTS FOR THE SYNTHESIS OF DRUG-LOADED ORDERED MESOPOROUS SILICA

P. Lacroix-Desmazes[a], M. Bathfield[a], J. Reboul[a], E. Molina[a],
M. Mathonnat[a,b], A. Phimphachanh[a,b], N. Marcotte[a], M. In[b], C. Gérardin[a]

[a]Institut Charles Gerhardt, UMR 5253 CNRS, UM, ENSCM. Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale. 34296 Montpellier Cedex 5, France.

[b]Laboratory Charles Coulomb, UMR 5221 CNRS, UM. University of Montpellier, 34095 Montpellier Cedex 5, France.

patrick.lacroix-desmazes@enscm.fr, http://www.icgm.fr/

Asymmetric poly(N-isopropylacrylamide)-*b*-poly(ethylene oxide) (PNIPAM-*b*-PEO) and poly(acrylic acid)-*b*-poly(ethylene oxide) (PAA-*b*-PEO) double hydrophilic block copolymers (DHBC), with short PNIPAM and PAA blocks, have been purposely synthesized by RAFT and ATRP controlled radical polymerizations.[1,2] On one hand, we will report on the reversible self-assembly of the thermosensitive PNIPAM-*b*-PEO copolymer in aqueous solution upon heating. In a one-pot eco-friendly process in water, self-assembly of the DHBC in the presence of ibuprofen, followed by sol-gel synthesis, directly led to the successful formation of ibuprofen-loaded ordered mesostructured silica showing a distinctive (slow) drug release profile.[2,3] On the second hand, we will describe the reversible self-assembly of the anionic PAA-*b*-PEO copolymer in water in the presence of oppositely charged cationic drugs. Drug-polymer electrostatic complexes have been characterized and further used as new structure-directing agents in sol-gel synthesis. Hence, ordered mesoporous silica loaded with aminoglycoside antibiotics have been prepared in a single step ensuring optimal drug loading and pH-dependence of the drug release from the materials.[2,4]

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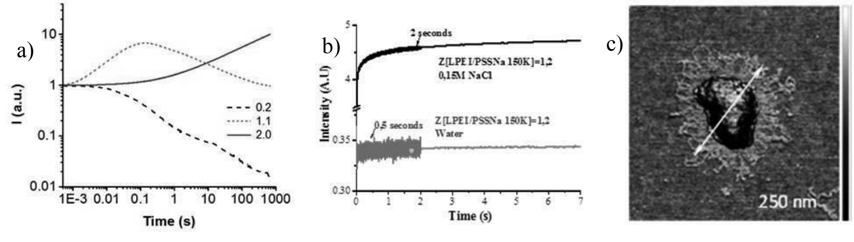
OP-28

STOPPED-FLOW STUDY OF MACROMOLECULAR ASSEMBLIES OF POLYELECTROLYTES

X. Liu[a,b], M. Haddou[a,b], E. Ibarboure[b], J. Giermanska[a], J. P. Chapel[a],
C. Schatz[b]

[a]Centre de Recherche Paul Pascal (CRPP), UPR CNRS 8641, Université Bordeaux, 33600 Pessac, France
[b]Laboratoire de Chimie des Polymères Organiques, Bordeaux INP, CNRS, Université de Bordeaux - 33600 PESSAC, France
(schatz@enscbp.fr, www.lcpo.fr)

The complexation of oppositely charged polyelectrolytes through Coulomb interaction is an extremely fast process with typical reaction times lying in the millisecond range. In order to gain insight into the early stages of the complexation we used in this work the stopped-flow technique with a light scattering detection. The study has revealed very different behavior according to the type of polyelectrolyte complexes we formed. In case of strongly interacting systems giving rise to solid-like precipitate, scattering intensities initially increase monotonically with time and then quickly stabilize at certain values. In case of weakly interacting systems giving rise to liquid-like coacervate, a rich variety of behavior corresponding to the different stages of the coacervation processes has been highlighted and modelled with a set of master equations. The morphology of the complexes obtained through stopped-flow mixing was also studied by light and small-angle neutron scattering and AFM. Interestingly, the stopped-flow mixer allows to prepare PECs in very fast and much more reproducible manner than bench methods.



Time dependence of the scattering light intensities upon stopped-flow mixing of PAA/PDADMAC (a) and PEI/PSS (b) complexes at various molar charge ratios. AFM analysis of PEI/PSS complexes highlighting the formation of a core shell structure (c).

OP-29

SELF-ORGANIZATION OF CATIONIC pH- AND THERMO-RESPONSIVE COPOLYMERS

E. Deniau[a], M. Rabyk[b], L. Billon[a], O. Borisov[a], M. Hruby[b], P. Stepanek[b]

[a]Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et Materiaux, Universite Pau et Pays de l'Adour, France

[b]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Czech Republic

(elise.deniau@univ-pau.fr)

The goal of the present work is to show that novel type of multi-responsive cationic block-gradient copolymers can exhibit reversible pH- and temperature-controlled association in aqueous media leading to diverse nano-aggregates.

The dimensions and the morphology of the aggregates can be affected by external stimuli, such as temperature, ionic strength and pH provided that the copolymers comprise ionic pH-sensitive or/and thermo-sensitive monomer units. Such properties of the copolymer nano-assemblies make them attractive for multiple applications ranging from nano-electronics to nano-medicine. There are literature reports that block copolymer micelles with cationic coronae can be used as efficient transfection agents due to their ability to make reversible complexes with DNA.

Here, we will present the structural properties of supra-molecular assemblies formed in aqueous solutions of cationic pH- and thermo-sensitive block-gradient copolymers comprising one block of poly(dimethylaminoethyl acrylate) P(DMAEA) and one or two terminal blocks with a gradient sequence of styrene and DMAEA monomer units. We will show that because of the gradient sequence of the terminal blocks such copolymers are capable of reversible association giving rise to micellar-like aggregates in aqueous solutions as a function of both pH and temperature. The cationic charge of the PDMAEA blocks opens the perspective to use this smart copolymer nanostructures as non-viral vectors for genetic material.

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OP-30

EXPLORATION OF SELECTIVE DECORATION OF JANUS SILICA PARTICLES WITHIN POLYMERIC PATTERNED PORE ARRAYS

P. Yang, W. Sun, J. Huang, L. Ding

Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 315211, China (sunwei@nbu.edu.cn)

Janus particles, especially amphiphilic ones, are known to be highly active when put into interfacial self-assembly processes[1]. However, experimental reports on employing Janus particles as interfacial stabilizer to establish functional structures are rather limited. In this work, amphiphilic Janus silica particles were prepared by selective chemical treatment on the particle "colloidosomes"[2]. Different ways (decoration of Au nanoparticles, interfacial adsorption test) were used to confirm on the acquirement of the Janus character of the particles. Upon successful synthesis of amphiphilic Janus particles, they were employed in the breath figures method for the first time. It turned out that by using the Janus particles, a regularly arranged pore array could be easily obtained. Characterization of the morphology of the patterned structure shows that Janus particles were densely located on the interior wall of the entire holes, forming a finer particle arrays comparing to the case of hydrophilic particles[3,4]. The result indicates that Janus particles show optimized behavior when they are involved in the interfacial self-assembly processes. For further works, by choosing Janus particles with functional features, selective functionalization of porous films could be achieved with high efficiency and great ease using this method.

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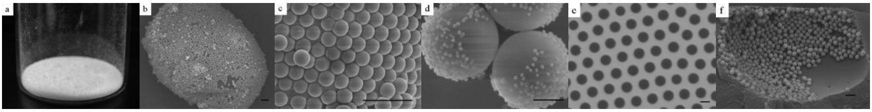

Fig.1 (a) digital photograph and (b, c) SEM images of colloidosomes made by the emulsion method using wax and silica particles; (d) SEM images of Janus particles partially labeled with Au nanoparticles; (e) Top and (f) cross-sectional SEM images of porous films fabricated from Janus particle-assisted BF process. The scale bars are 2 μm (b, c, e, f) and 250 nm (d).

OP-31

PLANET-SATELLITE NANOSTRUCTURES FROM STAR POLYMERS AND GOLD NANOPARTICLES

C. Rossner[a], V. Roddatis[b], O. Glatter[c], P. Vana[a]

[a]Institut für Physikalische Chemie, Georg-August-Universität Göttingen,
Tammannstraße 6, D-37077 Göttingen, Germany

[b]Institut für Materialphysik, Georg-August-Universität Göttingen,
Friedrich-Hund-Platz 1, D-37077 Göttingen, Germany

[c]Institut für Anorganische Chemie, Technische Universität Graz,
Stremayrgasse 9/V, A-8010 Graz, Austria

(crossne@gwdg.de, www.mmc.chemie.uni-goettingen.de)

Because of their stability and facile surface modification, gold nanoparticles (AuNPs) are attractive building blocks for the exploration of strategies that assemble these nanoscale objects into hierarchically ordered structures. We recently demonstrated the assembly of two types of AuNPs into planet–satellite arrangements using RAFT star polymers (Figure 1).[1]

This presentation will report results from a systematic variation of star polymer arm number and discuss consequences of the macromolecular architecture on the distance scaling behavior in planet–satellite structures. Analysis of interparticle distance data in the dried state (via TEM) is complemented by experiments in colloidal dispersion (employing SAXS). Interestingly, different results are obtained in these situations, and possible reasons for this will be discussed. Results from STEM-SI mapping of macromolecular species within these structures, which lead toward a better understanding of the particle assembly mechanism, will also be presented.

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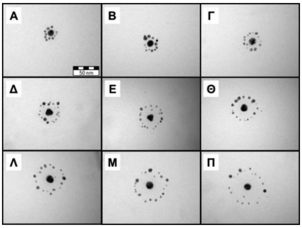

Figure 1. Planet–satellite structures from gold nanoparticles of different sizes with star polymers of increasing molar mass.

OP-32

SPECTRALLY ACTIVE POLYMERIC MICELLES

A. J. Harnoy, I. Rosenbaum, M. Buzhor, L. Frid, M. Segal, G. Slor,
N. Weber, L. Peles, G. Goldener, R. J. Amir*

Department of Organic Chemistry, School of Chemistry, Faculty of Exact Sciences, and the Tel Aviv University Center for Nanoscience and Nanotechnology, Tel-Aviv University, Tel-Aviv 69978, Israel.

**amirroey@tau.ac.il*

The rising demand for advanced drug delivery systems that can release their active molecular payload selectively at the target tissue has motivated the development of stimuli-responsive polymeric nanocarriers. The next major challenge in the field is to design delivery systems that are capable of self-reporting their activation by changing their spectral properties upon disassembly and release of the molecular cargo. To address this challenge we present a new molecular design of labeled enzyme-responsive amphiphilic hybrids that are composed of a linear hydrophilic polyethyleneglycol (PEG) block and a dendron with enzymatically cleavable lipophilic end-groups as the hydrophobic block. The utilization of a mono-disperse dendron as the enzyme-responsive block, allowed us to study the disassembly mechanism with high molecular resolution and to adjust the disassembly rates by simple tuning of the dendritic structures.

Based on these modular hybrids, we designed the next generation of smart polymers that are capable of changing their spectral properties in parallel with the enzymatically induced structural change. We will demonstrate the ability to induce both fluorescence and magnetic resonance responses by introduction of the proper labeling moieties. These hybrids open the way for advanced diagnostic and therapeutic systems that can self-report their location and degree of activation.

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Keywords: Block-copolymers, self-assembly, smart materials, Enzyme-responsive, nanocarriers for drug delivery

OP-33

TWO-DIMENSIONAL POLARIZATION MICROSCOPY REVEALS POLYMER CHAIN SELF-ORGANIZATION IN THIN FILMS OF CONJUGATED POLYMERS

D. Täuber[a], W. Cai[b], Y. Xia[b], O. Inganäs[b], I. G. Scheblykin[a]
[a]*Chemical Physics, Lund University, Sweden*
[b]*Biomolecular and Organic Electronics, Linköping University, Sweden*
(daniela.tauber@chemphys.lu.se www.lund.chemphys.lu.se/groups/sms)

2D polarization microcopy[1] is able to reveal local polymer chain orientations of thin conjugated polymer films. In a liquid spread TQ1 film we find domains with similar polymer chain orientation exceeding 1 mm along and hundreds of µm perpendicular to the spreading direction, see Figure 1. By correlating the fluorescence intensity, modulation depth (M_{em}) and phase angle (θ_{em}) of photoluminescence polarization, we obtain information on local structure changes. Comparing the microstructure seen in the M_{em} and θ_{em} images, from blends of TQ1 and N2200 before and after annealing, we find an increased local polymer alignment upon annealing in agreement with results from X-ray and force microscopy[2]

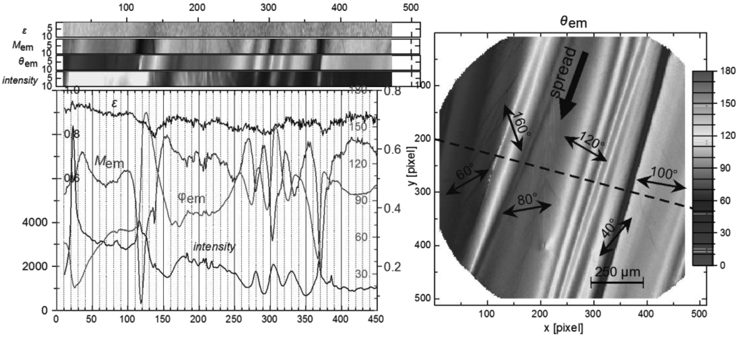

Figure 1 (right): θ_{em} image: macroscopic liquid spreading direction as well as phase angles at particular positions are marked by blue arrows; (left): ε, θ_{em}, M_{em}, and fluorescence intensity along cross section (dashed blue) indicated in θ_{em} image.

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NOTES

POSTERS

P-01

SYNTHESIS OF POLYMERIC BIOSURFACTANTS FROM VEGETABLE OILS AND CHARACTERIZATION OF INTERFACIAL PROPERTIES FOR COSMETIC PRODUCTS

S. M. Lee[a], J. Y. Lee[a], B. J. Kim[b], K. Y. Choi[b], K. M. Lee[b], J. C. Lim[a]
[a]*Dept.of Chemical Eng., Dongguk Univ., Seoul 100-715, Korea*
[b]*AK ChemTech Central Research Lab., DongGu, DaeJeon 300-824, Korea*
(jongchoo@dongguk.edu)

In this study, phospholipid polymeric biosurfactants with excellent biodegradable characteristics were synthesized from renewable vegetable oils for cosmetic products applications. The structure of the resulting products was elucidated by FT-IR and NMR spectroscopies and environmental compatibility of the synthesized polymeric surfactants such as biodegradability and acute oral toxicity was also evaluated. The interfacial properties of synthesized polymeric surfactants have been evaluated such as CMC, static and dynamic surface tensions, interfacial tension, wetting property, emulsification activity, and foam property. The prescription test in shampoo formulation prepared with new polymeric biosurfactants indicated better sensory feeling and excellent foaming ability compared with that prepared with silicon.

Acknowledgement

This work was supported by "the Technology Innovation Program“(10050496, Development of environment friendly biocompatible surfactants and their related products derived from natural resources derived) funded by the Ministry of Trade, Industry & Energy, Korea.

P-02

THE NEXT GENERATION OF MUCOADHESIVE BIOPOLYMERS

F. Laffleur

Department of Pharmaceutical Technology, Institute of Pharmacy, Center for Molecular Biosciences Innsbruck, University of Innsbruck, Innrain 80/82, 6020 Innsbruck, Austria
(Flavia.Laffleur@uibk.ac.at)

Biomaterials have gained immense interest in the pharmaceutical research in the last decades. Hyaluronic acid a carbohydrate and mucopolysaccharide was chemically modified in order to achieve and establish a promising platform for buccal drug delivery. Aim: Novel biomaterial was tested for its potential for buccal drug delivery. Background: Polysaccharide hyaluronic acid (HA) was chemically modified with cysteine ethyl ether (CYS). By immobilization of the thiol bearing ligand on the polymeric backbone the thiolated bioconjugate HA-CYS was obtained. Methodology: Mucoadhesive, permeation enhancing and stability potential as well as mechanical, physicochemical properties further mucoadhesive strength, swelling index and residence time were investigated. The developed thiolated bioconjugate displayed enhanced mucoadhesiveness on buccal mucosa as well as permeation behavior and polymer stability. The near neutral pH and negative cytotoxicity studies indicated their non-irritability and biocompatible nature with biological tissues. Further, the model drug sulforhodamine 101 was incorporated to determine its drug release profiles. Results: The synthesized thiomer showed no toxicity. The mucoadhesion of thiolated hyaluronic acid on buccal mucosa was significantly improved in comparison to unmodified one. The biomaterial showed 2.5-fold higher stability in polymer structure. The release of sulforhodamine in presence of thiolated hyaluronic acid was 2.3-fold increased compared to hyaluronic acid. Conclusion: Thus, the promising results encourage further investigations and exploitation of this versatile polysaccharide. So far, hyaluronic acid was not evaluated for buccal drug delivery.

P-03

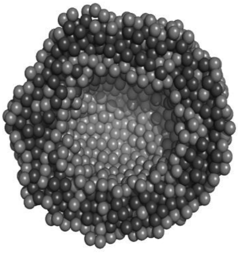
INTRAMOLECULAR SEGREGATION WITHIN AMPHIPHILIC MACROMOLECULES: CYLINDERS & VESICLE

V. V. Vasilevskaya, A. A. Glagoleva

A. N. Nesmeyanov Institute of Organoelement Compounds RAS Vavilova ul. 28, 119991, Moscow, Russia

(vvvas@polly.phys.msu.ru)

The paper deals with macromolecules which are amphiphilic on a level of a single monomer unit in sense that each monomer unit ***A*** contains both hydrophilic and hydrophobic group and could be represented [1] as a "dumbbell" **H**-graft-**P**, consisting of **H** and **P** beads, connected by a fixed-length bond. Depending on the values of energetic parameters of interactions, a variety of thermally stable conformations emerge in that system [1-2]: necklace-like structures consisting of intramolecular micelles, disk-like and cylindrical globules. The later has almost linear dependence of macromolecule gyration radius R_G on its degree of polymerization N: $R_G \sim N^{\nu}, \quad \nu \sim 1$.



Vesicle-like globule (cross-section)

In opposite case [3], when macromolecule is immersed in the selective solvent, which is good for backbone ***H*** groups and poor for **P** side groups, vesicle-like globules are formed by long chains even in the excess of solvent (see Figure). Such globules have spherical shape, hollow interior and thin bilayer shell. For such globules the following scaling dependence is valid: $R_G \sim N^{1/2}$.

Acknowledgements. *The research was supported by Russian Scientific Fund (n. 14-13-00745).*

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P-04

STOCHASTIC LAG TIME IN NUCLEATED LINEAR SELF-ASSEMBLY

N. Tiwari[a], P. van der Schoot[a,b]

[a]*Group Theory of Polymers and Soft Matter, Eindhoven University of Technology, The Netherlands*
[b]*Institute for Theoretical Physics, Utrecht University, The Netherlands*
(n.tiwari@tue.nl, www.imc.cas.cz)

Protein aggregation is of great importance in biology, e.g., in amyloid fibrillation. The aggregation processes that occur at the cellular scale must be highly stochastic in nature because of the statistical number fluctuations that arise on account of the small system size at the cellular scale. We study the nucleated reversible self-assembly of monomeric building blocks into polymer-like aggregates using the method of kinetic Monte Carlo. Kinetic Monte Carlo, being inherently stochastic, allows us to study the impact of fluctuations on the polymerisation reactions. One of the most important characteristic features in this kind of problem is the existence of a lag phase before self-assembly takes off, which is what we focus attention on. We study the associated lag time as a function of the system size and kinetic pathway. We find that the leading order stochastic contribution to the lag time before polymerisation commences is inversely proportional to the system volume for large-enough system size for all nine reaction pathways tested. Finite-size corrections to this do depend on the kinetic pathway.

P-05

QUEBEC CENTER FOR ADVANCED MATERIALS (QCAM)

P. Fiurasek[a], T. van de Ven[a], A. Soldera[b]

[a]*McGill University, 801 rue Sherbrooke Ouest (Québec) Canada, H3A 0B8 (www.csacs.mcgill.ca)*

[b]*Université de Sherbrooke, 2500, boul. de l'Université, Sherbrooke (Québec) Canada, J1K 2R1(http://www.cqmfscience.com)*

QCAM has been created this year 2016, resulting of the merger of CSACS (Center for Self-Assembled Chemical Structures, 2002) and CQMF (Centre Québécois sur les Matériaux Fonctionnels, 2008). Through a collaborative spirit and by respecting the values of both groups, we expect this new entity, to become a leader in materials science across Quebec, Canada and at the international level.

The principal objectives of QCAM are:

To establish Quebec as THE reference research cluster for advanced materials.

To promote collaborations and enable projects not realizable by one single research group.

To provide research students with the multidisciplinary training and access to state-of-the-art research facilities maintained by a team of professionals.

Build national and international research partnerships with academic, governmental and industrial collaborators.

Enable technology transfer to leverage economic growth.

The main research axes of QCAM are:

1) Supramolecular and self-assembled structures;

2) Polymers;

3) Biointerfaces;

4) Nanosciences and nanotechnologies;

5) Energy;

6) Biomaterials;

7) Environment/sustainable development;

8) Smart materials.

P-06

INTERPARTICLE INTERACTIONS BETWEEN DIBLOCK COPOLYMER GRAFTED NANOSHEETS

S. Gupta, P. Chokshi

Department of Chemical Engineering, Indian Institute of Technology,
Hauz-Khas, New Delhi 110016, India

Polymer-particle interactions can be effectively utilized to produce composites that possess physico-chemical properties superior to that of neat polymer. The incorporation of fillers with dimensions comparable to polymer chain size produces composites with extra-ordinary properties owing to very high surface to volume ratio. The dispersion of nanoparticles is achieved by inducing steric repulsion realized by grafting particles with polymeric chains. A comprehensive understanding of the interparticle interaction between these functionalized nanoparticles plays an important role in the synthesis of a stable polymer nanocomposite. With focus on incorporation of clay sheets in a polymer matrix, we theoretically construct the polymer mediated interparticle potential for two nanosheets grafted with polymeric chains. The self-consistent field theory (SCFT) is employed to obtain the inhomogeneous composition field under equilibrium. We present the results of SCFT calculations of the interaction potential curve for two grafted nanosheets immersed in the matrix of polymeric chains of dissimilar chemistry to that of the grafted chains. The interaction potential is repulsive at short separation and shows depletion attraction for moderate separations induced by high grafting density. It is found that the strength of attraction well can be tuned by altering the compatibility between the grafted and the mobile chains. Further, we construct the interaction potential between two nanosheets grafted with diblock copolymers with one of the blocks being chemically identical to the free polymeric chains. The interplay between the enthalpic interaction between the dissimilar species and the entropy of the free chains gives rise to a rich behavior in interaction potential curve. Moreover, the self-assembly of two blocks of the diblock copolymer influences the interparticle potential curve obtained for the two separate cases of free chains being chemically similar to either the grafted block or the free block of the grafted diblock chains.

P-07

STARCH BASED NANOPARTICLES

D. C. Leite[a], T. Hellweg[b], N. P. da Silveira[a]

[a]Institute of Chemistry, Federal University of Rio Grande do Sul, Bento Gonçalves Ave. 9500, 90650-001 Porto Alegre, RS, Brazil
[b]Faculty of Chemistry, Bielefeld University, Universitätstrasse 25, 33615 Bielefeld, Germany (nadya@iq.ufrgs.br)

Starch nanoparticles have earned special attention due to their submicron size, which improves dispersibility and adaptability for multiple functions due to their greater surface area.[1] In order to study and explore the crystal structure and chain organization of starch and its nanoparticles, X-ray scattering techniques have been used. In this work, corn starch nanoparticles were formed using a nanoprecipitation procedure in absolute ethanol, resulting in particles with narrow size distribution (R_h= 70.9 ± 2.5 nm). Wide-angle X-ray scattering (WAXS) patterns for native corn starch (CS) and corn starch nanoparticles (NS) were acquired, and different profiles could be found. According to our results, CS presents the typical A-type allomorph profile with characteristic peaks at 10.3, 12.4 and 15.9 nm^{-1}, while NS presents B + V-type patterns, with characteristic peaks at 3.8, 11.6, 15.1 and 16.3 nm^{-1}. This result may be attributed to an increase in starch bachbone mobility within the amorphous regions, leading to a molecular re-organization.[2] Regarding the crystallinity index,[3] CS and NS exhibited 36.5% and 55.3%, respectively. It has been suggested that cleavage of starch chains in the amorphous regions allowed reordering of the chain segments to give a more crystalline structure.[4] Similar crystallinity index results and chain re-organization patterns are reported by others authors.[2,5,6]

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P-08

PREPARATION OF POROUS FUNCTIONAL FILMS BY MICROPHASE SEPARATION OF BLOCK COPOLYMERS

S. Schoettner[a], H.-J. Schaffrath[b], M. Gallei[a]

[a]*Macromolecular Chemistry Department, Technische Universität Darmstadt, Alarich-Weiss-Straße 4, 64287 Darmstadt, Germany*

[b]*Paper Technology and Mechanical Process Engineering, Technische Universität Darmstadt, Alexanderstraße 8, 64283 Darmstadt, Germany*

Block copolymers consist of two or more polymer segments covalently connected to each other and they have attracted enormous attention due to their unique capability of forming fascinating nanostructures in the bulk or by self-organization in solvents. Moreover, such polymers can be addressable by external triggers representing a unique class of building blocks for the generation of novel materials.[1,2] Herein, we focus on the synthesis of polymeric materials, which contain a polar block segment, *i.e.* poly(hydroxyl ethylmethacrylate) (PHEMA). The non-solvent induced phase separation (NIPS) process is applied for nano porous structure formation on hydroxyl-containing paper substrates in order to gain access to flexible integral asymmetric membranes featuring a selective isoporous layer (see Figure 1).[3] By taking advantage of the functional groups, the soft template can be subjected to sol-gel-chemistry for the preparation of *e.g.* titanium-functionalized pores. These novel functional hybrid materials have the potential to act as *e.g.* sensors or switchable membranes.

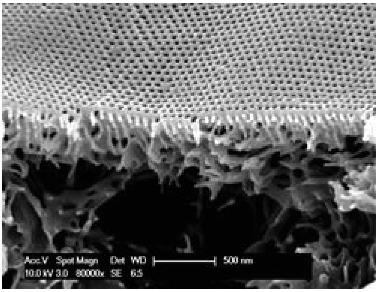

Figure 1: SEM image of functional block copolymer isoporous membranes.

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P-09

MICRO-PHASE SEPARATION OF RENEWABLE MULTIARM BLOCK COPOLYMERS FOR THERMOPLASTIC ELASTOMERS

Y.-W. Kim[a,b]

[a]*Center for Biobased Chemistry, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon, 34114, Korea*

[b]*Department of Green Chemistry and Environmental Biotechnology, University of Science & Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon, 34113, Korea*
(ywkim@krict.re.kr, www.imc.cas.cz)

We report herein the preparation and characterization of multi-arm star block copolymer TPEs based on renewable biomass, which comprise poly(ε-decalactone)−poly(L-lactide) (PDL−PLLA) arms, using one-pot, two-process ring-opening transesterification polymerization (ROTEP) of ε-decalactone (DL) and L-LA. We also expected to exhibit particular tendencies of hydrodynamic radius, morphologies, and thermal/mechanical properties for the renewable multiarm star block copolymers at fixed volume fraction of hard block and designed high molar mass, which were finally served as TPEs in comparison with the linear ABA triblock copolymer. Atomic force microscopy (AFM) showed that this system had thinner PLLA hard domains and thus more compact microphase-separated structures by increasing n. Additionally, small-angle X-ray scattering (SAXS) measurements at $T_m < T$ indicated that the samples had clearer morphology for hexagonally packed cylinders and decreased domain spacing with increased n. The uniaxial tensile experiments demonstrated mechanically enhanced properties for the multiarm specimens even having limited crystallinity due to the tighter microphase-separated structure and the pinning effect in the cross-linked polymer systems.

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P-10

MONODISPERSE POLYMERIC PARTICLES: SELF-ASSEMBLING AND LUMINESCENCE PROPERTIES

E. Tomšík[a], N. Shevchenko[b], G. Pankova[b], T. Ukleev[c], A. Sel'kin[c]

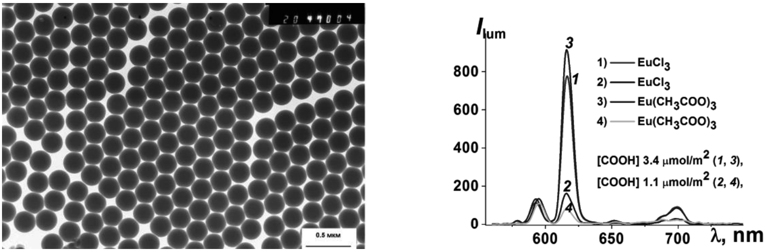
[a]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

[b]Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoi pr. 31, 199004 St. Petersburg, Russia

[c]Ioffe Physical-Technical Institute of Russian Academy of Sciences, 26 Polytekhnicheskaya, 194021 St. Petersburg, Russia
(natali.shevchenko29@gmail.com, www.hq.macro.ru)

Development of polymeric particles self-assembling into 3D ordered structures is urgent need for both fundamental investigation and practical application. Recently, there has been a great interest in dye-containing particles and their ordered arrays as novel nanomaterials for optoelectronics. Hence, there is a drive to develop new methods for modification of monodisperse polymeric particles with dyes.

For this purpose monodisperse core-shell particles were prepared by emulsion copolymerization. At the last polymerization step methacryloyl o-aminobenzoic acid were introduced in the particle shells, because functional groups were shown to be convenient for the linking of rare earth ions on the particle surface. Thin 3D ordered films of the particles were fabricated, fluorescence and reflection spectra were studied. SEM was applied to prove well-ordered structure of the films.



a b

Figure 1. TEM images of particles (a) and fluorescence spectra of 3D ordered films (b).

P-11

SELF-ASSEMBLED HIGHLY ORDERED POLY(3,4-ETHYLENEDIOXYTHIOPHENE) FILMS WITH HIGH ELECTROCHEMICAL CAPACITANCE AND ELECTROCHROMIC EFFICIENCY

E. Tomšík, N. Gospodinova

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(tomsik@imc.cas.cz, www.imc.cas.cz)

Poly(3,4-ethylenedioxythiophene) is one of the recognized faradaic capacitors. It is believed that poly(3,4-ethylenedioxythiophene) with high specific capacitance (180 F/g) can be obtained only by electrochemical synthesis due to opportunity to control the growth of the poly(3,4-ethylenedioxythiophene) film (1). For this reason the electrochromic efficiency of poly(3,4-ethylenedioxythiophene) being closely related to its faradaic behavior has been studied up to now only for electrochemically prepared polymer. We have shown that using suitable chemical synthetic technique it is possible to obtained self-assembled highly ordered poly(3,4-ethylenedioxythiophene) films with specific capacitance of 210 F/g. Electrochromic efficiency of these films is also very promising.

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P-12

MICROPHASE SEPARATION OF NOVEL AMPHIPHILIC MULTIBLOCK COPOLYMERS

S. Schmidt, P. Vana

Institute of Physical Chemistry, Georg-August-University Goettingen,
Tammanstraße 6, 37077 Goettingen, Germany
(sonja.schmidt1@stud.uni-goettingen.de)

Novel amphiphilic multiblock copolymers of styrene and *N*-isopropylacrylamide were synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerizations using polytrithiocarbonates as chain transfer agent. The composition of PS (polystyrene) and PNIPAM (poly(*N*-isopropylacrylamide)) were determined by ^{1}H-NMR, and the block numbers were obtained by comparing the molecular weights of multiblock copolymers to that of cleaved products as determined by size exclusion chromatography (SEC).

m-PS$_{103}$-PNIPAM$_{308}$ multiblock copolymer possesses number-average molecular weight (M_n) of 54.600 g/mol and the polydispersities ($Đ$) is around 1.5. The microphase separation of this multiblock copolymer system was investigated by atomic force microscopy (AFM). Measurements showed that the equilibrium morphology is a soft transition in comparison to diblock copolymers. The formation of morphologies depends on the composition of the multiblock copolymers and their molecular weight needs to be >50.000 g/mol.

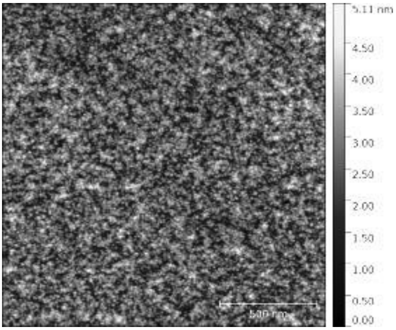

Figure 1: AFM height profile of m-PS$_{103}$-PNIPAM$_{306}$ after annealing for 3 days at 160°C.

P-13

PEG-*b*-PCL DIBLOCK COPOLYMERS: OPTIMIZATION OF THE SYNTHESIS TOWARDS LOW PDI FOR TARGETED SELF-ASSEMBLED STRUCTURES

E. Konishcheva, W. Meier

Chemistry Department, University of Basel, Klingelbergstrasse 80, Basel, 4056, Switzerland

Hollow polymeric spheres, or polymersomes, are very advantageous and attractive 3D self-assembled structures due to their ability to keep a desired environment for the encapsulated molecules. When polymersomes with encapsulated molecules are applied as a drug delivery system, the choice of suitable self-assembling polymers severely narrows, as the polymer should be biocompatible and biodegradable. A prominent example of such polymer is amphiphilic poly(ethylene glycol)-*block*-polycaprolactone (PEG-*b*-PCL) diblock copolymer. Under fixed self-assembly conditions PEG-*b*-PCL is able to self-assemble in aqueous solution into polymersomes and other 3D-structures depending on the hydrophilic weight fraction and the block length.[1,2] Consequently, targeted self-assembly into a certain 3D-structure generally requires PEG-*b*-PCL with a certain block length and rather narrow polydispersity. For example, PEG(2K)-*b*-PCL(9.5K) with PDI = 1.14 forms predominantly mesoscale vesicles[1], whereas similar copolymer PEG(2K)-*b*-PCL(9K) but with higher PDI = 1.42 forms mostly mesoscale worms[2] under similar self-assembly conditions.

In this work, we describe how to obtain a monodisperse PEG-*b*-PCL (PDI < 1.1) by optimizing its well-known synthesis catalyzed by $SnOct_2$. We also discuss the effect of aging of $SnOct_2$ on overall kinetics of the synthesis. Furthermore, we compare self-assembled structures formed by monodisperse PEG-*b*-PCL (PDI < 1.1) with its polydisperse analogues (PDI > 1.1) to gain insight into the effect of the PDI on the self-assembled structures.

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P-14

HYBRID HYPERBRANCHED POLYMER/MESOPOROUS SILICA FOR PROLONGED DRUG DELIVERY

H. D. M. Follmann[a,c], O. N. Oliveira Jr[a], R. Silva[b], T. Asefa[c]

[a]São Carlos Institute of Physics, University of São Paulo (USP), - PO Box 369, CEP 13566-590, São Carlos, São Paulo, Brazil

[b]Department of Chemistry, State University of Maringá (UEM) - Av. Colombo 5790, CEP 87020-900 – Maringá, Paraná, Brazil

[c]Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854, USA

The easy, versatile chemical functionalization of mesoporous silica opens the way for numerous possibilities of use, since its chemical and physical properties can be tailored.[1,2] For instance, such mesoporous silica can be employed for prolonged, controlled release of drugs,which is useful for the pharmaceutical industry in the search of innovative systems displaying localized drug delivery.[3] In this study, we report on the synthesis of nanomaterials based on mesoporous silica, grafted with groups that may be applied for controlled drug release. Dexamethasone, a glucocorticoid used clinically as an anti-inflammatory and immunosuppressive agent,[4] was incorporated into the internal walls of pores in mesoporous nanoparticles via hydrophobic interactions. The *in vitro* release of dexamethasone from hybrid aerogels containing the silica nanoparticles was prolonged up to two months, with the release time being amenable to control by varying the density of the aerogel.

Keywords: Silica Mesoporous, dexamethasone, controlled release.

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P-15

PHASE SEPARATION IN WATER SOLUBLE PORPHYRIN/POLYMER HYBRID SYSTEMS

J. Labuta[a], N. Velychkivska[b], L. Starovoytova[b], M. Hrubovský[c],
H. Kouřilová[c], L. Hanyková[c], I. Krakovský[c], J. Lang[d], S. Ishihara[e],
J. P. Hill[f]

[a]International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan (Labuta.Jan@nims.go.jp)
[b]Department of NMR Spectroscopy, Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovského Sq. 2, 162 06 Prague, Czech Republic.
[c]Department of Macromolecular Physics, Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic
[d]Department of Low Temperature Physics, Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic
[e]Frontier molecules group, International Center for Materials Nanoarchitectonics (MANA), NIMS
[f]Supermolecules Group, MANA, NIMS, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Porphyrins are widely studied functional dyes that play essential role in living organisms (e.g. photosynthetic antenna and reaction center, heme protein as an oxygen carrier, etc.). Previously, we have shown that porphyrins can be used for various sensing properties[1-5] such as enantiopurity detection, selective detection of anions, determination of trace water impurities in organic solvents, etc. However, most of these properties are achievable only in organic solvents (chloroform, DMSO, etc.). Therefore, we have synthesized water soluble porphyrin/polymer derivatives **P**s (Fig. 1a), which exhibit reversible response to various external stimuli such as temperature (phase separation, Fig. 1b), pH (colorimetric response, Fig. 1c) and solvent composition (co-nonsolvency). These effects will be discussed in presentation.

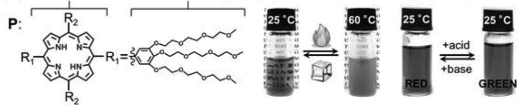

Fig. 1. (a) Structure of porphyrins Ps. Temperature (b) and pH (c) response.

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P-16

ASSEMBLY OF VIRUS-LIKE NANOPARTICLES IN PRESENCE OF A FLEXIBLE POLYION. A MOLECULAR DYNAMICS SIMULATION INVESTIGATION

D. G. Angelescu, D. Caragheorgheopol

Institute of Physical Chemistry "Ilie Murgulescu", Romanian Academy,
Spl. Independentei 202, Bucharest, Romania
(dangelescu@hotmail.com, www.icf.ro)

At a basic description a virus consists of a protein shell, often referred to as a capsid, which surrounds an encapsulated nucleic acid. Cargo molecules such as synthetic polymers or inorganic nanoparticles can be also encapsided to form virus-like nanoparticles. The spherical viruses possess icosahedral symmetry mostly and they self-assemble from numerous copies of one or slightly different proteic units, called capsomers. Furthermore, the capsids carrying flexible single stranded genome assemble spontaneously from free capsomers in the presence of the oppositely charged genome only.

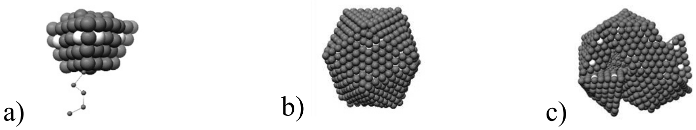

Figure 1. a) A single triangular capsomer and snapshot of b) fully and c) aberrant developed virus-like nanoparticle showing the assembly of 20 capsomers around a linear flexible polyion.

The role of a flexible polyion in the assembly of a virus-like nanoparticle with icosahedral symmetry has been investigated using molecular dynamics simulation on a coarse-grained model. The polyion is modeled by a linear bead-spring chain, and the capsomers i) possess a flexible triangular-trapezoidal shape given by the harmonic bond-like connectivity among the soft-sphere constituents, ii) carry explicit charges located along a short chain grafted on the capsomer surface and iii) present attractive sites on each lateral side (Fig. 1a). Apart from fully developed icosahedral viral nanoparticles (Fig. 1b), the simulations also predict disordered assemblages enclosing either completely or partially the polyion (Fig. 1c).

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P-17

COBALT FERRITE NANOPARTICLES IN NEMATIC LIQUID CRYSTALS

C. Cîrtoaje, C. Stan, E. Petrescu

Politehnica University of Bucharest, No. 313 Splaiul Independenței,
no. 313, sector 6, RO-060042, Bucharest, Romania
(cristina.cirtoaje@upb.ro, www.physics.pub.ro)

Cobalt ferrite nanoparticles dispersed in nematic liquid crystals (NLC) act as a common ferrofluid in isotropic state[1]. In crystalline phase, a completely different behavior is noticed, partly due to the strong anchoring of nematic molecules on the nanoparticles surface[2]. Analysis of nanoparticles organization in nematic matrix was performed immediately after the sample preparation and later at different temperatures. The samples were also subjected to several sonicating sessions confirming the system's stability both in planar and twisted oriented cell. The results revealed extremely stable ferromagnetic nanoparticles chains that could not be broken when subjected to thermal or mechanical processes that usually destroy the nematic alignment.

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P-18

ALIGNED NANOPARTICLES IN NEMATIC LIQUID CRYSTALS

C. Cîrtoaje, E. Petrescu

Politehnica University of Bucharest, No. 313 Splaiul Independenței, no. 313, sector 6, RO-060042, Bucharest, Romania
(cristina.cirtoaje@upb.ro , www.physics.pub.ro)

Nematic liquid crystals (NLC), commonly used in displays, have other unique properties that make them extremely interesting for technical applications. Experimental results performed on different mixtures of nematic liquid crystals and carbon nanotubes, ferroelectric or ferromagnetic nanoparticles revealed considerable differences in electric conductivity[1], Freedericksz transition thresholds[2, 3] or response time[4]. We noticed that carbon nanotubes insertion in NLC leads to a 400% of the sample conductivity for homeotropic cell and 100% for planar alignement. When ferroelectric nanoparticles are inserted in NLC, both parallel and perpendicular anchoring of nematic director to particle's surface are possible so the Freedericks transition threshold can vary in both directions. Ferromagnetic platelets in nematics show the most amazing behavior as they suddenly align themselves with the rubbing directions of homogenous prepared glass plates forming long stable chains. An analysis of the interaction energies between LC molecules and nanoparticles based on theoretical models[5, 6] is made and its conection with electro-optical or magneto-optical properties of each mixture is presented.

***Acknowledgements**: The authors acknowledge the financial support through the grants of the Romanian Governmental Representative at JINR and scientific projects No.96/15.02.2016 item 64.*

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P-19

AMPHIPHILIC BRANCHED COPOLYMERS OF N-VINYLPYRROLIDONE – A PROMISING DRUG CARRIERS

N. A. Obraztsova, S. V. Kurmaz

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka 142432, Russia
(obrazcova-nadezh@mail.ru, www.icp.ac.ru)

There are a large number of hydrophobic drugs. Their study and application requires water-soluble form which can be obtained by chemical modification or encapsulation in different carriers. In the latter case, the structure of the active substance and its biological properties remain unchanged. The most suitable carriers are micelles formed by amphiphilic block copolymers (BCs). However, the preparation of BCs is a multi-step laborious process that often requires the use of biologically incompatible substances (metal complexes, alkoxylamines *etc.*). In the present study we first investigated branched copolymers of N-vinylpyrrolidone (VP) obtained by radical copolymerization as drug carriers.

Amphiphilic VP copolymers form micelles in selective solvent due to hydrophilic VP units and hydrophobic methacrylate ones[1]. It was shown by TEM and DLS that copolymers form reverse micelles in toluene, direct micelles in isopropanol and water, and vesicles in water/isopropanol mixtures. We can control the micelles size (30 – 160 nm) by changing the copolymer composition or solvent nature. Using C_{60}, doxorubicin as model drugs it was found that micelle core is capable to solubilize drugs. After drying such structures and dissolving in water drug remains in carrier. Their size ranged from 100 to 150 nm. Cryo-TEM images show that drug-loaded micelles retain micelle-like structure and the drug is encapsulated in its core. It was found using IR-spectroscopy, DSC, SAXS, TEM, SEM that the encapsulated substances retain its structure. In experiments with HeLa cells using a fluorescence microscopy it was shown that polymer particles comprising a hydrophobic fluorescent dye are noncytotoxic and these can penetrate into the cells and deliver encapsulated substance.

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P-20

ELECTROCHEMICAL GENERATION OF TRANSITION METAL NANOPARTICLES (Fe, Co, Ni) FOR CATALYTIC OLIGO- AND POLYMERIZATION

A. F. Khusnuriyalova[a,b], A. V. Sykhov[a], E. V. Gorbachuk[a,b], R. I. Vagizov[a], D. G. Yakhvarov[a,b]

[a]A. M. Butlerov Institute of Chemistry of Kazan Federal University
Kremlyovskaya str., 18, 420008 Kazan, Russia

[b]A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center of the Russian Academy of Sciences. Arbuzov str., 8, 420088 Kazan, Russia
(aliya15071993@mail.ru)

This work is devoted to elaboration of new techniques for preparation of active catalysts for ethylene oligo- and polymerization processes based on transition metal nanoparticles bearing sigma-bonded organic groups. We have found that electrochemical reduction of coordinatively unsaturated transition metal (Fe, Co, Ni) complexes formed by 2,2'-bipyridine leads to the formation of metal nanoparticles which can be used for catalytic purposes. The monitoring of the transition metal nanoparticles generation was performed by *in situ* EPR-spectroelectrochemistry and Small-Angle X-ray Scattering (SAXS).

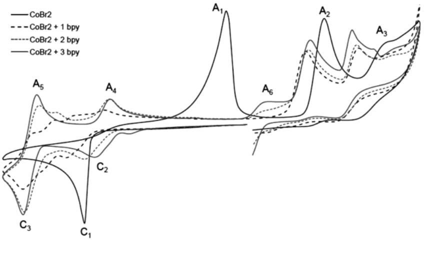


Figure 1. Cyclic voltammogram of Co^{2+} in the presence of 2,2'-bipyridine

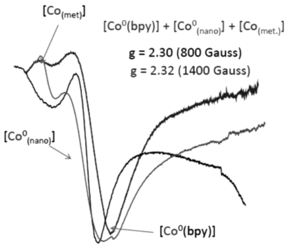


Figure 2. EPR spectra of the electrochemically generated nanoparticles

This work is financially supported by the British Petroleum Exploration Operating Company Limited (grant № C40-15) and the special program of the Russian Foundation for Basic Research and the Government of the Republic of Tatarstan (project № 15-43-02667).

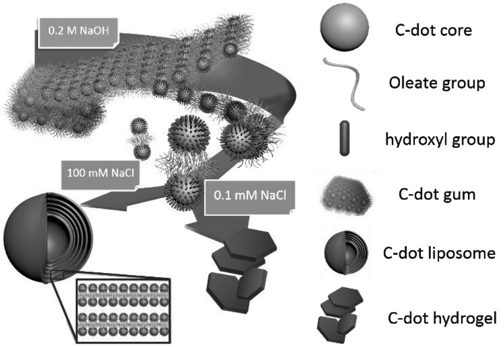
P-21

STRATEGIES FOR FORMATION OF VARIOUS SUPERSTRUCTURES OF CARBON DOTS

T.-H. Chen, Y.-T. Tseng, C.-H. Chen, H.-T. Chang

Department of Chemistry, National Taiwan University, Taipei, 10617, Taiwan
(aspirinchang@gmail.com, www.imc.cas.cz)

Large-scaled self-assembly of supermolecule can initiate new materials with both of monomers and collective properties, and the designable special optical with mechanical and thermal dynamic properties had attracted numerous attentions. However, the large-scaled superstructures of sub-nanometer materials such as carbon dots had been discussed limitedly. Herein, we utilized the oleated glycerol as precursor to build up a gum-like 3D carbon dots (gum C-dots) superstructure in one-step method. Furthermore, we manipulated this superstructure as templates to modify the C-dot to form the Janus particle which has amphiphilic property. The Janus particle obtained from C-dot assembly with different superstructures like liposomes (C-dot liposome), hydrogels (C-dot hydogel) etc. was well arranged by rational design through adjusting the concentration of salt in C-dot solution due to the geometry of the oleate groups on the surface of C-dots that are highly affected by the ionic strength.



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P-22

THE EFFECT OF NANOPARTICLE NON-UNIFORMITY ON THE RATIO OF RADIUS OF GYRATION AND HYDRODYNAMIC RADIUS

P. Kratochvíl, M. Netopilík

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

The ratio of the radius of gyration, obtained by static light scattering, and the hydrodynamic radius, obtained by dynamic light scattering, is a routine experimental technique for the assessment of nanoparticle shape. The potential effect of particle non-uniformity is mostly not considered. In this communication, we demonstrate that, even with medium particle non-uniformities, it is advisable to apply appropriate corrections. The values of the correction factors are offered in a diagram for various particle shapes, and two types of particle-size distributions and their widths.

P-23

MOLECULAR SIMULATIONS OF FLOWER-LIKE MICELLES AND MICELLAR GELS

L. Nová, F. Uhlík, P. Košovan

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 00 Praha 2, Czech Republic (Lucie.Nova@natur.cuni.cz)

We studied the system of block copolymers of the type hydrophobic – hydrophilic (polyelectrolyte) – hydrophobic. This system may form flower-like micelles or micellar gels, depending on conditions. We used Hybrid Monte Carlo method in the reaction ensemble (our in-house implementation). This method enables more efficient sampling of the configuration space then using molecular dynamics only. We are able to govern the system features in the simulated system - its micellization and gelation - by means of varying concentration, pH and ionic strength.

We observed lower association numbers with higher ionization (higher K_A) and higher association numbers with lower ionization (lower K_A). We observed, as expected, that with adding salt intramolecular connections (loops, micellization) are preferred prior to the intermolecular connections (bridges, gelation).

P-24

pH-RESPONSIVE BEHAVIOUR OF LINEAR WEAK POLYELECTROLYTE

L. Nová, P. Košovan, F. Uhlík

Department of Physical and Macromolecular Chemistry, Faculty Science,
Charles University in Prague, Hlavova 8, 128 00 Praha 2, Czech Republic
(Lucie.Nova@natur.cuni.cz)

We studied the pH-responsive behaviour of long linear weak polyelectrolytes by means of Hybrid Monte Carlo simulations in the reaction ensemble. The chains consist of 100 beads. Each bead is a single weak acid, which can dissociate with the probability according to given K_A. The solvent was modelled as dielectric continuum. Several solvents (permittivities) were applied. No salt was added. The concentration effects on the titration and pH were studied. The problems of local pH and finite size effect are discussed. The shape and size properties of the chain are described by the dependence of Radius of gyration on the degree of dissociation α, pH and solvent permittivity.

P-25

THE STRUCTURE OF CYCLIC MULTIBLOCK COPOLYMERS

A. Kuriata, A. Sikorski

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
(sikorski@chem.uw.edu.pl)

The structure of single multiblock cyclic copolymers in a selective solvent was studied[1]. For this purpose we developed and studied an idealized model of polymer rings at various solvent conditions1. All atomic details were suppressed and chains were represented as a sequence of identical beads embedded to a square lattice. A simple square-well potential was used for polymer-polymer interactions[2]. An efficient Monte Carlo sampling algorithm using local and non-local changes of chain's conformation as well as the Replica Exchange technique were used to sample the conformational space. Simulation results concerning the structure of globules formed at low temperature were discussed and compared with theoretical predictions and the structure of linear copolymers[1,3]. Self-assembly in this polymer system was attributed to a competition between the architecture constraints and the minimization of polymer-solvent interface.

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P-26

BIOMIMETIC POLYMERSOMES THROUGH A SYMBIOSIS OF ORGANIC AND POLYMER CHEMISTRY

J. Gaitzsch[a,b], V. Chudasama[b], G. Battaglia[b], W. Meier[a]

[a]*Department of Chemistry, University of Basel, Klingelbergstrasse 80,*
4056 Basel, Switzerland
[b]*Department of Chemistry, University College London, 20 Gordon St,*
London WC1H 0AH, United Kingdom
(jens.gaitzsch@unibas.ch)

The chemical versatility polymers is one of the major benefits of polymersomes.[1] However, even more potential can be unlocked if polymer chemistry is combined with organic chemistry to obtain the polymer.[2]
Unlike natural vesicles, polymersomes usually have a surface without any domains (patches), which represents a major drawback. We accomplished stable domains by synthesising a miktoarm star terpolymer based on dibromomaleimide. Translated from organic chemistry it proved to serve as a highly stable linker, enabling patchy polymersomes (see figure).[2]
It is often required to label vesicles with dyes or proteins. From the ligation chemistries available, we found the TAD chemistry, recently translated from organic chemistry, to be the most efficient.[3]

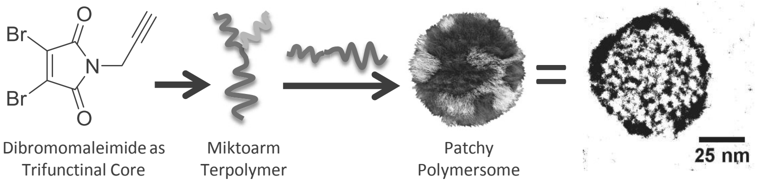

Figure 1: A dibromomaleimide core molecule is transformed to a miktoarm terpolymer in efficient reactions. Patchy polymersomes are then accomplished using this polymer.

These results show the benefit if organic and polymer chemistry are combined to give the desired properties of the final vesicles.

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P-27

MINERALIZED ASSEMBLED NANOPARTICLES FOR NITRIC OXIDE-MEDIATED CANCER THERAPY

H. J. Lee, D. E. Kim, S. C. Lee
Department of Maxillofacial Biomedical Engineering, School of Dentistry,
Kyung Hee University, Seoul 02447, South Korea
(schlee@khu.ac.kr)

We describe a calcium carbonate ($CaCO_3$) mineralization approach to generate pH-responsive nanocarriers that can stably load S-nitrosoglutathione (GSNO) and dissolve at acidic endosomes to trigger intracellular release of nitric oxide (NO). GSNO-loaded $CaCO_3$-mineralized nanoparticles (GSNO-MNPs) were prepared by an anionic block copolymer (PEG-Poly(L-aspartic acid))-templated mineralization. Ionic GSNO could be loaded *in situ* inside the $CaCO_3$ core during the mineralization process. The stability of GSNO shielded within the crystalline $CaCO_3$ core could be greatly enhanced.[1] The GSNO-MNPs triggered NO release at endosomal pH and an intracellular ascorbic acid level. Confocal microscopy demonstrated that the GSNO-MNPs could be dissolved at endosomal environments to release GSNO and sequentially generate NO through the GSNO reduction in the cytosol. As previously reported literature data, cell experiments demonstrated that NO release by the GSNO-MNPs efficiently improved therapeutic activity of doxorubicin.[2]

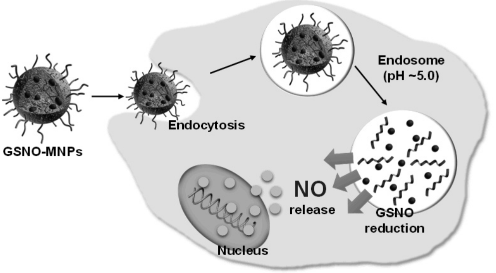

Fig. 1. Illustration for intracellular NO release from GSNO-loaded mineralized nanoparticle.

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P-28

CONFORMATIONAL BEHAVIOUR OF POLYMER CHAINS OF DIFFERENT ARCHITECTURES IN SOLVENT MIXTURES. DISSIPATIVE PARTICLE DYNAMICS STUDY

L. Suchá, Z. Limpouchová, K. Procházka

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague 2, Czech Republic
(Lu.GA.Sucha@gmail.com)

Specific preferential solvation of polymer chain is a general phenomenon which significantly affects the behaviour of polymers dissolved in solvent mixtures and plays an important role in a number of processes.

We studied the conformational behaviour of polymers affected by preferential solvatation of polymer chains in mixtures containing poorly miscible components. Polymer of various architectures (linear, star, dendrimer) were simulated in good solvent A with a small admixture of a slightly better solvent B (interacting favorably with the polymer and unfavorably with the majority solvent A).

We observed the polymer chain collapse caused by the minimization of the number of unfavorable A-B interactions and by the maximization of the number of A-A interactions. Depending on the strength of interaction, this observed collapse can lead to phenomenon called "cononsolvency".[1]

The polymer solutions were simulated via Dissipative Particle Dynamics (DPD) - off-lattice, coarse-grained method.[2]

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P-29

SELF-ASSEMBLED LIQUID-CRYSTALLINE AND NANO-CRYSTALLINE STRUCTURES OF POLYANILINE: SPECTRAL AND ELECTROCHROMIC SIGNATURES

N. Gospodinova, T. Skorokhoda, O. Kohut, E. Tomšík

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(gospodinova@imc.cas.cz, www.imc.cas.cz)

It is shown for the first time that self-assembled liquid-crystalline semiconducting polymer, polyaniline, manifests considerably higher extinction coefficient in all the oxidation states as well as substantially higher electrochromic efficiency (168 *versus* 52 cm^2/mC at 633nm) than the nano-crystalline one. The great potential of the nematic state of the organic semiconductors for the exciton and charge transport has been revived by us recently[1].

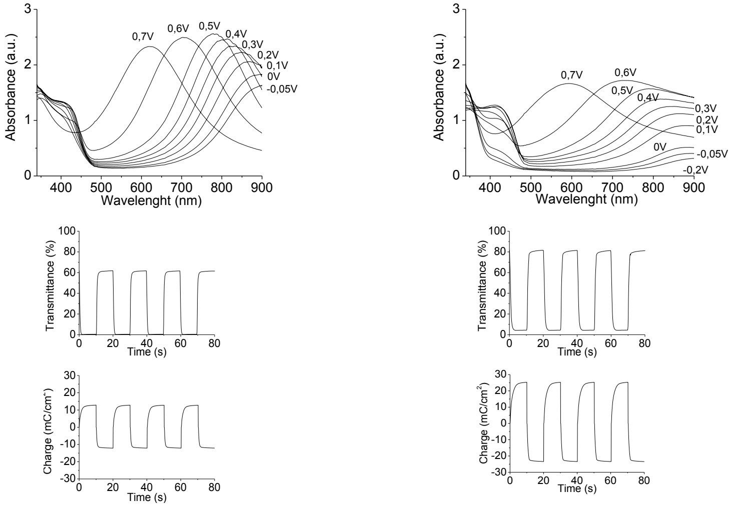

Figure 1. Optical absorption spectra at different potentials (top), transmittance curves at 633nm with corresponding chronoamperometry (bottom) for liquid-crystalline (left) and nano-crystalline (right) thin polyaniline film

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P-30

SELF-ASSEMBLY OF POLYMER GRAFTED NANOPARTICLES FOR 'MATRIX-FREE' POLYMER NANOCOMPOSITES

J. Choi, A. Kirakosyan, J. Im

Department of Materials Science and Engineering, Chungnam National University, Daejeon, Korea
(jihoonc@cnu.ac.kr)

Polymer-grafted nanoparticles show new opportunities for the 'matrix-free' polymer nanocomposites in which polymer brushes serve a dual purpose: first, to facilitate a more robust mechanical response, and second, to control the microstructure of the inorganic core by tuning the polymer brush architectures (i.e. molecular weight and grafting density). In addition, the steric forces imposed by the dense polymer brushes drive the preferential segregation of additional nano-scale fillers such as nano rods or nanotubes into the interfacial region between the polymer-grafted nanoparticles. Here we demonstrate that the control of the polymer brush architecture can facilitate a hierarchical nanostructures in 'matrix-free' polymer nanocomposites that provide a new platform for radar absorbing materials.

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P-31

SOLUBILISATION OF LINEAR HOMOPOLYMER CHAINS INTO ELECTROSTATICALLY CO-ASSEMBLED MICELLES. A DISSIPATIVE PARTICLE DYNAMICS STUDY

K. Šindelka, Z. Limpouchová, L. Suchá, K. Procházka

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43, Praha 2, Czech Republic
(karel.sindelka@natur.cuni.cz)

Nanoparticles with solvophobic core co-assembled from oppositely charged polymer chains can be utilised as nanocontainers for low molar compounds in various fields including targeted drug delivery or environmental applications (pollutant removal), because of their stimuli responsive properties.

We studied micelles self-assembled from hydrophobic positively charged homopolymer chains and diblock copolymer chains containing one negatively charged block and one neutral well soluble block and their interactions with short linear polymer chains. The solvophobic nature of added polymer chains leads to their encapsulation within the micelles.

The focus was placed on the effect of length and concentration of the solubilised polymer chains as well as their solubility and compatibility with the components of the micelles. We investigated the stability of such complexes and the amount of solubilised polymer chains.

The study was performed using a computer simulation method known as the dissipative particle dynamics.

Acknowledgements

This work was funded by the Czech Science Foundation grant number 13-02938S and by the Grant Agency of Charles University grant number 422216. Computational resources were provided by the CESNET LM2015042 and the CERIT Scientific Cloud LM2015085, provided under the programme " Projects of Large Research, Development, and Innovations Infrastructures."

P-32

SELF-ASSEMBLY OF PHENANTHRENE OLIGOMERS INTO NANOTUBES WITH LIGHT-HARVESTING PROPERTIES

C. D. Bösch, S. M. Langenegger, R. Häner

*Department of Chemistry and Biochemistry, University of Bern,
Freiestrasse 3, 3012 Bern, Switzerland*

Supramolecular polymerization enables the construction of highly organized chromophore arrays and thus is a method to build up artificial light-harvesting antennae.[1] In previous work we described the formation of a one-dimensional supramolecular polymer which absorbs light and effectively transfer the excitation energy to an acceptor.[2] Assembly of a two-dimensional light-harvesting antenna would increase the number of ordered chromophores for energy collection. In this poster we will present results for a 2,7-disubstituted phenanthrene oligomer which forms tubular structures in aqueous medium. Those assemblies are only weakly fluorescent but the addition of minute amounts of acceptor results in a strong increase of fluorescence. Figure 1 B) displays fluorescence intensities with and without incorporation of a pyrene-containing oligomer. Other aromatic compounds will be tested for their capability and efficiency to act as acceptor molecules.

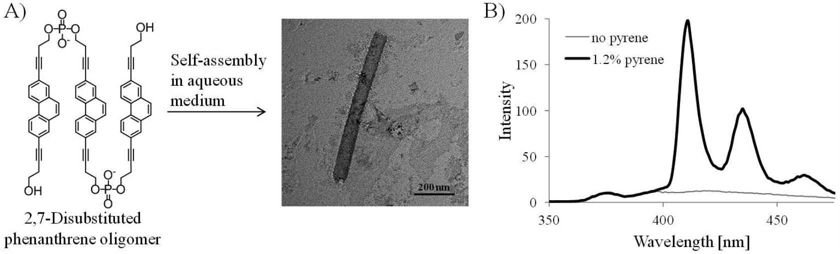

Figure 1: A) Chemical structure of 2,7-disubstituted phenanthrene oligomer and TEM image of supramolecular polymer. B) Fluorescence measurement of assembled phenanthrenes (grey) and in presence of 1.2% pyrene (black) upon excitation of phenanthrene.

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P-33

FOOD-GRADE CAPSULES BASED ON MICROFLUIDIC

J. C. Chang, E. Amstad

Materials Science and Engineering Section, École polytechnique fédérale de Lausanne, Switzerland

(jui-chia.chang@epfl.ch)

Motivation

Capsules are often used in food, for example, to protect active ingredients or to control their release [1]. They can conveniently be made from double emulsion templates. One method that offers good control over the size and composition of double emulsions is microfluidics. We employ this methods to produce food-grade capsules that are soft but mechanically robust.

Experiment

We produce food-grade capsules from water-in-oil-in-water double emulsion templates that we assemble using microfluidics [2]. To make capsules soft, we fabricate the shell from sunflower oil and stabilize it using food-grade surfactants. We tune the mechanical properties of the shell as well as its permeability by adjusting the shell thickness, and surfactant composition. By choosing the right surfactant, capsules can be stable for months. Then in the future, by adding some responsive agent in the oil shell so that we can control released the encapsulation of active compounds inside capsules.

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P-34

NMR STUDY OF TWO TYPES OF THERMORESPONSIVE POLYMER SYSTEMS IN AQEOUS MEDIA

R. Konefał, J. Spěváček

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

Thermoresponsive polymers are class of materials that respond to changes in temperature. Along with the changes at the macromolecular level, dramatic phase or property changes occur.[1]

We used NMR spectroscopy to study two types of polymer systems containing thermoresponsive component (poly(*N*-isopropylacrylamide) (PNIPAm) or poly(2-ethyl-2-oxazoline) (PEtOx)) in D_2O solutions. First type were PNIPAm-clay nanocomposite hydrogels.[2] ^1H NMR spectra and spin-spin relaxation T_2 measurements were used for characterization of interactions of redox initiator system and NIPAm monomer with the clay both without and in the presence of the PNIPAm polymer. Significant effects which could affect structure-mechanical properties of the PNIPAm-clay nanocomposite hydrogels were found.

Second type were ABC block copolymers poly(ethylene oxide) (PEO)-*b*-PEtOx-*b*-(poly(ε-caprolactone) (PCL)) and ABC_2 block copolymers PEO-b-PEtOx-b-$(PCL)_2$ which were synthesized with constant length of PEO (44 units) and PEtOx (252 units) blocks, and various length of PCL blocks (35-131 units). Micellar nanoparticles of block copolymers were prepared by nanoprecipitation method. Measurements of temperature dependences of integrated intensities in high-resolution ^1H NMR spectra enabled us to determine the fraction of polymer units with significantly reduced mobility and subsequently to obtain information on the phase transition for all studied samples. The results depend on terpolymer architecture and important role of PCL blocks was revealed. Information on behavior of water molecules during the phase transition was obtained from T_2 relaxation experiments.

***Acknowledgements**: Support by the Czech Science Foundation (projects 15-13853S and 13-23392S) is gratefully acknowledged.*

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P-35

MECHANICAL PROPERTIES OF MULTIGRAFT COPOLYMERS PREPARED BY AN UP-SCALABLE SYNTHESIS APPROACH

R. Schlegel[a], H. Budde[b], U. Wendler[b], M. Bartke[b], M. Beiner[a,c]

[a]*Fraunhofer-Institut für Mikrostruktur von Werkstoffen und Systemen IMWS, Walter-Hülse-Str. 1, 06120 Halle(Saale), Germany*
[b]*Fraunhofer Pilotanlagenzentrum PAZ, Value Park A74, 06258 Schkopau*
[c]*Naturwissenschaftliche Fakultät II, Martin-Luther-Universität Halle-Wittenberg, Heinrich-Damerow-Str. 4, 06120 Halle (Saale), Germany*
(ralf.schlegel@imws.fraunhofer.de, www.imws.fraunhofer.de)

This work focuses on the mechanical characterization of rubbery tetrafunctional polyisoprene(PI)-*graft*-polystyrene(PS) multigraft copolymers prepared by an up-scalable anionic synthesis approach. To evaluate the mechanical performance, tensile and multiple hysteresis tests at different strain rates and at different maximum strains were applied. The data were analyzed based on standard parameters (Young's modulus, tensile strength, strain at break) and parameters related to the molecular structure (cross-link and entanglement density as well as softening) determined based on a non-affine tube model of rubber elasticity and a softening model.[1] Various multigraft copolymers with PS-grafts having a molecular weights of about M_w = 3, 6 and 9 kg/mol and 2 to 7 tetrafunctional branch points per macromolecule were investigated. Remarkable high strains at break and high tensile strengths, e. g. 11.4 N/mm² at 1472 %, 7.1 N/mm² at 1817 %) or 6.1 N/mm² at 2000%, were determined for self-assembled PI-*graft*-PS multigraft copolymers having at least three branch points. The mechanical characterization under cyclic loading revealed i) improvements in crosslink modulus G_c and entanglement modulus G_e for multigraft copolymers with large number of branch points and ii) a strain rate dependence of the entanglement modulus G_e and nearly strain rate independent values of crosslink modulus G_c.

***Acknowledgment**: This work was supported by the Federal Ministry of Education and Research (BMBF, Germany) in the frame of the project VIP0258 / 03V0343.*

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P-36

ENHANCEMENT OF TENSILE STRENGTH OF MULTIGRAFT COPOLYMERS - INFLUENCE OF BLENDING AND PEROXIDE CROSS-LINKING

R. Schlegel[a], N. Mahmood[b], H. Budde[c], U. Wendler[c], M. Beiner[a,b]

[a]*Fraunhofer-Institut für Mikrostruktur von Werkstoffen und Systemen IMWS, Walter-Hülse-Str. 1, 06120 Halle(Saale), Germany*

[b]*Naturwissenschaftliche Fakultät II, Martin-Luther-Universität Halle-Wittenberg, Heinrich-Damerow-Str. 4, 06120 Halle (Saale), Germany*

[c]*Fraunhofer Pilotanlagenzentrum PAZ, Value Park A74, 06258 Schkopau (ralf.schlegel@imws.fraunhofer.de, www.imws.fraunhofer.de)*

This work presents two approaches to enhance the mechanical performance of novel thermoplastic elastomers being polyisoprene(PI)-*graft*-polystyrene(PS) multigraft copolymers prepared by an up-scalable anionic synthesis route.

Solution blending of multigraft copolymers with low and high number of PS-grafts per macromolecule was used to study the influence of composition on the tensile properties. Further, a series of chemically cross-linked multigraft copolymers was prepared using different amounts of 1,4-bis(tert-butylperoxy)diisopropylbenzene (0.4, 0.8 and 1.2 wt.%).

Tensile tests show that a pronounced enhancement of the strain at break is observed in multigraft copolymer blends when increasing the concentration of the component having a high number of branch points while the tensile strength (σ_M) is less affected. Moreover, it has been found that small amounts of cross-links can significantly increase σ_M while the high strain at break values are mostly preserved. This shows that both strategies can be used to improve the mechanical properties of multigraft copolymers.

Acknowledgment: *This work was supported by the Federal Ministry of Education and Research (BMBF, Germany) in the frame of the project VIP0258 / 03V0343.*

P-37

AGGREGATION BEHAVIOR OF SODIUM DODECABORATE

A. Zhigunov[a], P. Matějíček[b], A. Kuklin[c], Yu. S. Kovalev[c,d]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic (zhigunov@imc.cas.cz, www.imc.cas.cz)*

[b]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic*

[c]*Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research,Russia*

[d]*Moscow Institute of Physics and Technology, Russia*

Aggregation behavior of for a wide range of concentrations of anionic boron hydrides was observed by small angle x-ray scattering (SAXS). For our study, we have chosen boron clusters B12 ($[B_{12}H_{12}]^{2-}$) with Na cations. The aggregation origin of these water-soluble boron clusters is still under discussion.

Boron cluster B12 is a symmetric object with delocalized charge. The aggregation behavior of such clusters is size and polarity dependent. Based on results obtained from different techniques (NMR, cryoTEM, conductometry, colorimentry, SAXS, WAXS) we propose a model which comprises two levels of aggregation. Correlation peak at $q = 1.2$ Å^{-1} arises with concentration increase. This peak corresponds to the distance ~5 Å and probably represents the lowest possible distance between boron clusters. The observed distances are in agreement with crystallographic results obtained by Terrence J. Udovic et al. [1, 2]. Another level of association, is seen as structure peak at $q = 0.36$ Å^{-1} for the concentrations started from 0.6M and higher. The aggregation is a result of concurrent electrostatic repulsion and minimizing energy due to hydrophobic nature of B12.

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P-38

SELF-ASSEMBLY FORMATION OF NH_4TiOF_3 MESOCRYSTALS: CONTROL SHAPE AND SIZES VIA LENGTH AND RATIO OF POLY(ETHYLENE GLYCOL)S

O. Boytsova[a,b], A. Sadovnikov[b], A. J. Sutherland[a]

[a]*Aston University, Birmingham, B4 7ET, UK*

[b]*Kurnakov Institute of Inorganic Chemistry Russian Academy of Sciences, Moscow, 119991, Russia (o.boytsova@aston.ac.uk)*

Mesocrystals (MCs) are a relatively newly described class of self-assembled materials with fantastic potential. Based on natural crystallisation phenomena, chemists have developed a working model of MC formation whereby polymers can be used to form organized inorganic structures with great success [1-2]. This said, the shape, period, size and morphology of self-organized structures (MCs) generated in this manner show strong structural dependence upon the polymer used. As such these unique substances have the potential to revolutionise materials/devices containing inorganic components. Applications are myriad and include building materials, solar cells, new biomimetic materials, and electronic devices etc [3-4].

We demonstrate that it is possible to obtain MC of NH_4TiOF_3 using a non-classical method employing a gel of $(NH_4)_2TiF_6$ and H_3BO_3 with poly(ethylene glycol)s PEGs. Dimension of the MC “squares” and thickness decrease with the length of PEGs as well as with the concentration of polymer in basic solution. This arises as the polymer plays an important role in both the controlling hydrolysis of $(NH_4)_2TiF_6$ and the self-assembly processes, results were also confirmed by XRD, Raman, SEM, FTIR, TGA methods as well. By heat treatment the mesocrystals of NH_4TiOF_3 transform to well-oriented assemblies of anatase nanoparticles. A photocatalytic activity of the TiO_2 (anatase) mesocrystals has been demonstrated.

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P-39

SELF-ORGANIZATION OF TWO-DIMENSIONAL NANOPORES AND THEIR USE IN CELL GROWTH AND PLASMONICS

V. H. Fragal, E. H. Fragal, A. F. Rubira, R. Silva

Department of Chemistry, State University of Maringá (UEM) - Av. Colombo 5790, CEP 87020-900 – Maringá, Paraná, Brazil.

Self-organization of pores arrays can be obtained by breath figure phenomenon. Recently, we demonstrated the association of dynamic deposition method with breath figure phenomenon as an approach to control the pore size. Interestingly, fast casting process lead to nanopores with pore diameter that can be below 100 nm, what was for the first time reported to the self-formation of pores.[1] The nanoporous arrays obtained by the breath figure can be applied as substrates for cell growth, and the effect of their nanopore size on cell growth can be tuned according to the pore size. For instance, the change in the average pore size of the polymer films from 1.22 μm to 346 nm results in a three-fold increase in cell viability. In addition, the nanoporous surface can also be used as as a pathway to the creation of an ordered metallic surface containing hexagonal nanoholes' arrays. The obtained materials demonstrate to be extraordinary superior to nanostructured surfaces built by elaborated nanofabrication tools. The use of two-dimensional matrix produced a significant Raman signal, the highest enhanced factor (EF) factor ever reported for an Au substrate and a non-resonant species. All the substrates studies demonstrate EF in the order 108. These results are so close to the maximum EF estimated by theoretical studies, 5 x 108 for Au nanosphere arrays.

Keywords: Nanofabrication, Nanopores arrays, Breath Figure Method, Cell gowth, Plasmonics.

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P-40

SELF-ASSEMBLY OF RANDOM MULTIBLOCK COPOLYMERS: EFFECT OF SHORT BLOCK PENETRATION INTO “ALIEN” DOMAINS OF THE LAMELLAR PHASE

E. N. Govorun, A. V. Chertovich

Faculty of Physics, Lomonosov Moscow State University, Leninskie Gory 1-2, Moscow 119991 Russia (govorun@polly.phys.msu.ru)

We consider random multiblock copolymers of 50:50 composition with long blocks composed of N_{long} monomer units of size a and short blocks composed of N_{sh} units. The block type (short or long) is random with the probability p_{sh} for a short block and $1-p_{\text{sh}}$ for a long one. It is assumed that a lamellar structure is formed with alternating layers containing mostly A or B monomer units separated by an interfacial layer. Short blocks are in the interfacial layer or in “alien” domains (where only short blocks adjacent to two long blocks of another type can present). If one short block is in an “alien” layer, then not only blocks of size N_{long} are in their own phase, but also a joint block of the size $N_{\text{j}}=2N_{\text{long}}+N_{\text{sh}}$.

The number of joint blocks is always less than the total number of long blocks. Besides, their characteristic spatial size $\sqrt{N_{\text{j}}}a$ can be less than the thickness of the layer and they are not stretched. In that case, the conformational energy is calculated as a correction to the free energy of a chain in a homopolymer phase due to the end localization at a layer surface. The calculation method is similar to that for the conformational energy of blocks with both ends localized at a globule surface.[1] The free energy of the system is written down in the strong segregation limit and the equilibrium values of the parameters are found.

Short block presence in “alien” domains affects the surface tension and number of joint blocks. Therefore, the microstructure parameters for considered copolymers should be much more sensitive to the interaction parameter (temperature) in comparison with regular multiblock copolymers.

We appreciate the financial support from the Russian Science Foundation (project 14-13-00683).

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P-41

NANOCARRIERS SELF-ASSEMBLED FROM FUNCTIONALIZED POLYETHYLENIMINE FOR ANTICANCER DRUG DELIVERY

J. Yan, J. Cao, B. He

National Engineering Research Center for Biomaterials, Sichuan University, 29 Wangjiang Road, Chengdu 610064, Sichuan, People's Republic of China (bhe@scu.edu.cn)

Multiple functionalization of nanoparticles has attracted great interest in drug delivery, In this paper, polymeric amphiphiles of polyethyleneimine (PEI) and mPEG-CHO、PCL-CHO and pyrene-1-carboxal dehyde(Py-CHO) were synthesized via Schiff's reaction. The conjugates self-assembled into nanoparticles with pH-sensitivity to load anticancer drug doxorubicin (DOX), the nanoparticles were coated with hyaluronic acid (HA) for tumor targeting. The mean size of nanoparticles was about 100 nm and the stability of the nanoparticles was well in aqueous solution. The drug release of the nanoparticles was faster in the medium with pH 5.0 compared to pH 7.4 and the nanoparticles coated with HA showed faster disassembly. The nanoparticles exhibited an endosomal escape function to accelerate the release of DOX in cancer cells, which resulted in low IC50s to kill 4T1 breast cancer cells and HepG2 liver cancer cells *in vitro*. Meanwhile HA has specific recognition capability to transmembrane glycoprotein CD44, which is overexpressed on surfaces of cancer cells[1-4]. The nanoparticles coated with HA internalized in cells via endocytosis mechanism mediated by CD44 receptor to exhibit better delivery effect.

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P-42

POLYMERIC MICELLES WITH DIFFERENT TOPOLOGICAL ARCHITECTURES FOR DRUG DELIVERY

Y. Zhang[a], X. Peng[b], S. Li[a*], B. He[b]

[a]*School of Chemical Engineering, University of Sichuan, Chengdu, 610065, China*
[b]*National Engineering Research Center for Biomaterials, Sichuan University, Chengdu, 610064, China*
(lisai@scu.edu.cn)

A series of drug delivery systems of ABC miktoarm star polymers based on poly(ethylene glycol)(PEG), poly(ε-caprolactone) (PCL), poly(L-lactide acid) (PLLA) or poly(DL-lactide acid) (PDLLA) and their triblock copolymers were studied.[1,2] The structure, molecular weight and crystallization property[3] of these amphiphilic polymers were characterized by proton Nuclear Magnetic Resonance (^{1}H NMR), Gel Permeation Chromatography (GPC) and Differential Scanning Calorimeter (DSC). The miktoarm star polymeric micelles revealed better stability than the triblock copolymers micelles. The polymeric micelles containing PDLLA showed smaller size than those containing PLLA. No significant initial burst was observed in the drug release *in vitro*. The micelles were noo-toxic to cells. The Confocal Laser Microscopy (CLSM) as well as the flow cytometry demonstrated that the miktoarm polymeric micelles with PDLLA showed higher endocytosis than those with PLLA. The miktoarm star polymeric micelles containing PDLLA showed better anticancer activity. It is a promising carrier for anticancer drug delivery.

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P-43

FABRICATION OF FLEXIBLE CELLULOSE FILMS CONTAINING MARINE ORGANISMS

K. J. Jang, S. E. Hong, R. K. R. Yoon*

Chemistry Based Bio Hybrid Sensor Research Team(BK21 plus), Organic Nano Material Lab, Department of Chemistry, Hannam University, 1646 Yuseong-daero, Yuseong-gu, Daejeon, 305-811, KOREA
(kryoon@hnu.kr)

Flexible cellulose films were prepared by solution cast method containing of cellulose, fucoidan, chitosan, and gelatin. Used cellulose from *Styela Clava Tunics* (SCTC) was treated with sodium hydroxide, sulfuric acid and hydrogen peroxide for removing impurities and bleaching process.[1, 2] Used Fucoidan from *Saccharina japonica* was extracted from Deep Eutectic Solvents (DES) of choline chloride-ethlyene glycol (molar ratio of 1:2) as solvent.[3,4] The resulting flexible cellulose films containing marine organisms were characterized by OM (Optical microscopy), SEM (Scanning electron microscopy), FT-IR (Fourier Transform Infrared Spectroscopy), CA (contact angel), Instron(Tensile strength), TGA (Thermogravimetric Analysis), AFM (atomic force microscopy) and X-ray diffraction(XRD).

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P-44

SYNTHESIS AND SELF-ASSEMBLY OF BIODEGRADABLE MIKTOARM STAR COPOLYMERS μ-PEG-PCL-PLLA

X. Peng[a], Y. Zhang[b], Y. Chen[b], B. He[a*]

[a]*National Engineering Research Centre for Biomaterials, Sichuan University, 29 Wangjiang Road, Chengdu 610064 China*
[b]*College of Chemical Engineering, Sichuan University, 24 South 1st section, 1st Ring road, Chengdu 610065 China*
(bhe@scu.edu.cn)

Miktoarm star copolymers show special properties for its unique structure and composition, such as self-assembled in multicompartment micelles in water due to the three immiscible components[1], formed pH-sensitive polymersomes in water[2], unique bulk crystallization behaviors[3] etc.

We synthesized a well-defined miktoarm star copolymer μ-PEG-PCL-PLLA, which composed of three biodegradable arm chains. We found that the miktoarm star copolymer μ-PEG-PCL-PLLA can self-assemble into hollow vesicles in water. Using TEM and DSC (show in fig.1) we confirmed the self-assemble mechanism of μ-PEG-PCL-PLLA. The outer shell was formed by PLLA microcrystalline as skeleton and PCL filled the void.

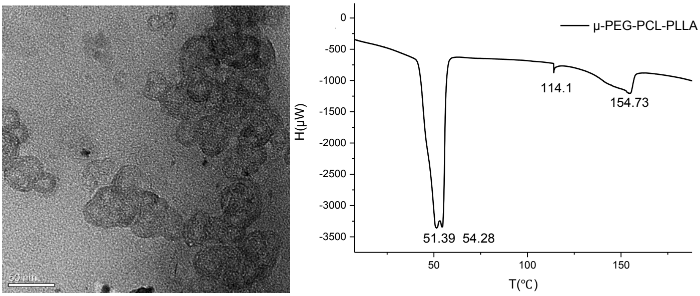

Fig.1 A. The morphology of the vesicles by TEM. B. The melting curves of μ-PEG-PCL-PLLA micelle lyophilized powder.

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P-45

NMR DIFFUSION AND RELAXATION TECHNIQUES AND MD SIMULATION – POWERFUL TOOLBOX TO DESCRIBE BINDING AND MOTIONS OF THE GUEST IN AN ANISOTROPIC METAL-ORGANIC FRAMEWORK

M. Peksa[a,b], S. Burrekaew[c], R. Schmid[c], F. Stallmach[b], J. Lang[a]

[a]*Charles University, Faculty of Mathematics and Physics, Dept. of Low Temperature Physics, V Holešovičkách 2, 180 00 Prague 8, Czech Rep.*

[b]*University of Leipzig, Institute of Experimental Physics I, Department of Physics of Interphases, Linnéstraße 5, Leipzig, 04105, Germany*

[c]*Ruhr-Universität Bochum, Inorganic Chemistry II, Organometallics and Materials Chemistry, Universitätsstr. 150, Bochum, 44780, Germany*

jan.lang@mff.cuni.cz

DMOF-1 is an anisotropic microporous metal-organic framework (MOF)[1] that displays a high adsorption capacity for CO_2. The crystal structure contains 1-dimensional channels of roughly nanometer size.

We performed an extended set of temperature dependent NMR diffusion and relaxation measurements on the adsorbed CO_2. In parallel, we carried out a long trajectory molecular dynamics (MD) simulation that was able to provide theoretical data complementary to the experimental ones. It was possible to localize the binding sites in the MOF and the corresponding orientation of the CO_2 guest. Next, the anisotropy of the translational diffusion of CO_2 inside of the microporous framework was determined[2,3]. Furthermore, three ^{13}C relaxation mechanisms active for CO_2 – the ^{13}C chemical shift tensor anisotropy, the ^{13}C-^{1}H intermolecular dipole-dipole interaction and the spin-rotation interaction were evaluated by means of their characteristic time autocorrelation functions. The respective correlation times on picosecond time-scale could be assigned to different modes of the CO_2 motion inside of the framework.

The concerted use of the experimental and theoretical techniques enabled a detailed description of behavior of the carbon dioxide guest in an anisotropic microporous polymer environment.

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P-46

PLURONIC-BASED CHEMILUMINESCENT EMULSION AS A NOVEL AGENT FOR ANTITUMOR THERAPY

A. V. Romanyuk, I. D. Grozdova, N. S. Melik-Nubarov

Department of Polymer Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, 1, bld. 40, Moscow, 119234, Russia
(andrey.v.romanyuk@gmail.com)

Photodynamic therapy (PDT) is a quickly emerging modality of treatment which employs the photochemical interaction of light, photosensitizer and oxygen. Photosensitizer localized in tumor and exposed to laser can transform molecular oxygen into highly toxic singlet state. The opacity of living body is a severe limitation of the technique. PDT is suitable only for tumors accessible to light guide.

We have designed a new light-free approach of photosensitizer excitation employing energy of chemiluminescent (CL) reaction between biochemically generated hydrogen peroxide and aromatic oxalates running in a living cell. This reaction is referred to as PeroxyOxalate ChemiLuminescent (PO-CL) reaction and might be a source of singlet oxygen. We have proved that this approach is successful in killing tumor cells pretreated with inducers of oxidative stress *in vitro*. For this purpose, we employed CL particles based on dimethylphthalate emulsion in water stabilized with Pluronic L64 and containing hematoporphyrin derivative as a photosensitizer. The active component was represented by oligooxalate synthesized via polycondensation of oxalyl chloride with oligo(propylene oxide) and bishenol A. Obtained particles possess negative zeta potential due to oxalate hydrolysis and exposition of carboxylic groups on the particles surface. To facilitate oligooxalate permeation through negatively charged cell membranes, its electrostatic complexes with poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) were prepared. Turbidimetry and dynamic light scattering studies revealed formation of electroneutral or slightly positively charged particles exhibiting high CL quantum yields. Anti-tumor activity of optimized CL formulations containing the polycation were tested in cell cultures.

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P-47

CONTROL OF CELL VIABILITY AND MULTIDRUG RESISTANCE BY AMPHIPHILIC NONIONIC BLOCK COPOLYMERS

A. V. Romanyuk[a], I. D. Grozdova[a], N. S. Melik-Nubarov[a], H. Frey[b]

[a]Department of Polymer Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, 1, bld. 40, Moscow, 119234, Russia

[b]Institute of Organic Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, Mainz, 55128, Germany

(grozdova@genebee.msu.ru)

Amphiphilic non-ionic block copolymers attract attention as bioactive agents. It is known that copolymers with intermediate hydrophobicity can induce MDR reversal in cancer cells and blood-brain barrier, while hydrophilic protect cells from mechanical stress. The present work was aimed to reveal structure-activity relationships in the series of non-ionic amphiphilic block copolymers containing propylene oxide, dimethylsiloxane or hydrocarbon radicals in their hydrophobic blocks and PEG or polyglycerol (PG) as hydrophilic blocks. Three biological effects are inherent for nearly all copolymers. Below CMC copolymers induce MDR reversal. At higher concentrations both hydrophilic and hydrophobic copolymers enhance cell viability. Further increase in polymer content leads to toxicity. Copolymer concentration sufficient for MDR reversal (C^{MDR}) correlates with the polymer ability to accelerate flip-flop in model lipid bilayers, indicating that interaction of PPO or PDMS hydrophobic blocks with lipid bilayer of cellular membrane underlies MDR reversion. PG-based block copolymers do no exhibit cell supporting activity. The copolymers bearing linear PEG blocks are able to enhance cell survival. The polymers with long PEG chains are effective as unimers while relatively hydrophobic polymers acquire this property only in the form of micelles. The effect may result from PEG interaction with oligosaccharides of glycocalyx. Copolymers cytotoxicity was defined by their HLB and is mainly governed by formation of pores in cell membranes. To avoid the undesired support of cancer cells, PEG-containing copolymers should be used at concentrations close to C^{MDR}. PG-based amphiphiles could be used as chemosensitizers in the full range of nontoxic concentrations above or equal to C^{MDR} without any risk to enhance survival of cancer cells.

P-48

SELF-ASSEMBLY OF *L*-PHENYLALANINE BASED DIPEPTIDE LOW MOLECULAR WEIGHT GEL FOR CHEMOTHERAPY

L. Xu[a], W. Gao[b], B. He[a*]

[a]*National Engineering Research Center for Biomaterials, Sichuan University, 29 Wangjiang Road, Chengdu 610064 China*

[b]*College of Chemistry & Materials Engineering, Wenzhou University, Wezhou 325035,China*

(bhe@scu.edu.cn;)

Low-molecular-weight organogels (LMOGs) have attracted considerable attention for their reversible capability and wide applications in drug release system[1]. The low-molecular-mass organic gelators self-assembled to form an orderly three-dimensional network through the non covalent bonds such as hydrogen bonding, π-π stacking interaction, van der Waals force, and so on[2]. And the organic solvents or water molecules are fixed in the three-dimensional network to form low-molecular-mass organic gels.

A novel *L*-phenylalanine based dipeptide LMOG were designed and synthesized. The structure of low-molecular-mass organic gelators was shown in Fig.1.C. The self-assembly mechanism and drug-loaded *in situ* gelation were explored. The therapeutic effect of the drug loaded gel was studied *in vivo*.

Fig.1 A. The SEM photos of xerogel(organogel in ethanol:13 mg/mL). B. The photo of gel loaded with doxorubicin in ethanol(10 mg gelators and 1 mg DOX in 1mL ethanol)

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P-49

LAYER-BY-LAYER SELF ASSEMBLY OF POLYELECTROLYTE MULTILAYERS ON BIODEGRADABLE SUBSTRATES WITH RESPECT TO CONTROLLED DRUG RELEASE

M. Marudova[a], I. Bodurov[a], S. Sotirov[a], Y. Uzunova[b], B. Pilicheva[b],
A. Viraneva[a], I. Vlaeva[c], G. Exner[a], T. Yovcheva[a]

[a]*Faculty of Physics, Plovdiv University "P. Hilendarski", 24 Tsar Assen str., 4000 Plovdiv, Bulgaria*
[b]*Faculty of Pharmacy, Medical University Plovdiv, 15A Vassil Aprilov Blvd., 4000 Plovdiv, Bulgaria*
[c]*University of Food Technologies, 26 Maritsa Blvd., 4000 Plovdiv, Bulgaria*
(margo@uni-plovdiv.bg)

The formation, chemical composition and physico-chemical properties of biodegradable and biocompatible polyelectrolyte multilayers (PEMs) from chitosan and xanthan are described. The PEMs are build-up at different pH and ionic strength onto activated by corona charging polylactic acid substrates using a layer-by-layer (LbL) self-assembling method. The successful deposition of the polyelectrolytes was proved by ATR FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). The film thickness, structure and surface topography were investigated by laser refractometry, SEM and AFM respectively. It was found out that the optimum pH value for the deposition process is 4.5 when the ratio of the positive charge on the chitosan molecules and the negative charge on the xanthan molecules is approximately 1 and the electrostatic interaction is performed by polyelectrolyte complexation. The PEMs could be deposited for a wide range of ionic strengths of the chitosan and xanthan solutions – from 0 mmol/L to 1000 mmol/L. Depending on the ionic strength different conformational states of macromolecules were observed. At low ionic strengths the macromolecules are in a stretched state and form a solid polyelectrolyte layers having a smooth structure. At higher ionic strengths the macromolecules occupy the conformation of random coil and the deposited layers are thicker and rough. Mucoadhesion is more pronounced for PEMs with ending xanthan layer and the increase of the number of layers leads to deterioration in the adhesion properties.

P-50

THERMORESPONSIVE *β*-GLUCAN-BASED POLYMERS FOR BIOMEDICAL APPLICATIONS

L. Loukotova*, M. Hruby

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
**corresponding author, e-mail: loukotova@imc.cas.cz*

Polysaccharides are fundamental components of organisms attracting increasing attention due to their extremely interesting biological functions. One of such polysaccharides is *β*-glucan, which has been widely known to show anti-cancer and anti-inflammatory activities.[1] Moreover, all living organisms are critically dependent on self-assembled nanostructures and thus polysaccharides have been broadly studied as substrates in formation of functional self-assemblies. Given the strong hydrophilicity of polysaccharides, their chemical modification is usually essential in order to allow them to form self-assemble in aqueous solution. Futhermore, the self-assembly as a response to external stimuli (temperature) could be usable in wide range of biomedical applications.

We synthesized and characterized new thermoresponsive *β*-glucan-based polymers grafted with poly(2-isopropyl-2-oxazoline-*co*-2-butyl-2-oxazoline) terminated with DOTA moieties. Starting *β*-glucan was extracted from bodies of Auricularia auricula-judae, which is high-molecular-weight and fully biodegradable. The synthesized derivatives were characterized by NMR, FT-IR, SLS, DLS and elemental analysis.

These bioinspired easy-to-synthesize artificial peptidoglycan-like polymers will be in future radio-labelled using chelation of radionuclide into DOTA-like moieties and subsequently used in brachytherapy.

Financial support of the Ministry of Health of the Czech Republic (grant # 15-25781A) and of the Grant Agency of the Czech Republic (grant # 16-02870S) is gratefully acknowledged.

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P-51

NANOSPECIES AFFECTING AMYLOID FORMATION

M. Holubová*, M. Hrubý

Department of Supramolecular Polymer Systems, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

corresponding author, e-mail: monik.holubova@gmail.com, www.imc.cas.cz

Amyloid is aggregated protein in the form of insoluble fibrils. All amyloids share some common physico-chemical features: fibrillar morphology, predominating secondary structure of β-sheet, birefringence after staining with Congo red, insolubility in common solvents and detergents and resistance against degradation by proteases. The amino acid sequence and structure of proteins associated with amyloidosis is highly variable[1]. Diseases associated with amyloid deposition are called amyloidoses and include, e.g., Alzheimer's disease or type II diabetes[2].

This research, utilizing hen egg-white lysozymes (HEWL) as a model system, is aimed at exploring substances, which could inhibit or promote amyloid formation. We investigated the influence of single-walled carbon nanotubes, fullurene-C_{60}, carbon quantum dots and poly(styrene-*alt*-maleic acid) sodium salt on formation of amyloid fibrils *in vitro*. Fibrils were detected by fluorescence of Thioflavin-T and absorbance of Congo red. Results were supported by transmission electron microscopy and birefringence of Congo red.

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P-52

NOVEL AMPHIPHILIC BLOCK-GRADIENT COPOLYMERS OF STYRENE AND 2-DIMETHYLAMINOETHYL ACRYLATE

M. Rabyk[a], E. Deniau[b], L. Billon[b], O. Borisov[b], M. Hruby[a], P. Stepanek[a]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*
(rabyk@imc.cas.cz, www.imc.cas.cz)
[b]*Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et Matériaux, Université Pau et Pays de l'Adour, France*

Amphiphilic block copolymers dissolved in aqueous solutions form a range of different nanostructures. Such nanoagregates can differ in size and morphology (micelles, nanospheres, lamellas, polymersomes etc.) and their formation strongly depends on the intra-molecular hydrophobic-hydrophilic balance.[1] Nevertheless, when the copolymer solution presents a dynamic equilibrium, the dimensions and even morphology of the nanostructures can be changed by varying of external parameters, such as pH, ionic strength and temperature.[2,3] The response to a specific external stimulus depends on the nature of monomeric unit (ionic pH-sensitive or/and thermo-sensitive) constituting the copolymer. These copolymers are attractive for a wide range of applications in different fields, such as nano-electronics, agro-chemistry and nano-medicine.

This work is dedicated to the preparation and the characterization of a novel type of amphiphilic block-gradient copolymers of styrene and 2-dimethylaminoethyl acrylate synthetized by nitroxide-mediated controlled radical polymerization. The determination of the reactivity ratios for the comonomers units and the characterization of the microstructure of the copolymers will be showed, as well as the study of their pH- and thermo-controlled self-assembly in water.

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P-53

THE CONFORMATIONAL AND HYDRODYNAMIC PARAMETERS OF NOVEL HYPERBRANCHED PYRIDYLPHENYLENE POLYMERS

A. S. Gubarev[a], N. V. Tsvetkov[a], E. V. Lebedeva[a], A. A. Lezov[a],
M. E. Mikhailova[a], L. I. Akhmadeeva[a], N. V. Kuchkina[b], E. S. Serkova[b],
Z. B. Shifrina[b]

[a]*St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034, Russia*

[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 119991, Russia*

(a.gubarev@spbu.ru)

Branched polymers (BPs) find numerous applications in technological processes. Also there are obvious advantages of such macromolecules over dendrimers (another branched molecule, which is monodisperse in regard to both size and structure), viz the facile synthesis and relatively low cost of final product. Furthermore BPs possess higher solubility and lower viscosity, than linear polymers of analogous structure.

The efficient and facile $A_6 + B_2$ approach has been proposed to synthesizing of hyperbranched pyridylphenylene polymers (HBPPP) using Diels-Alder polycycloaddition of the first-generation, six-functional pyridine-phenylene dendrimer (A_6) and the aromatic bis(cyclopentadienone)s (B_2) [1]. The newly synthesized HBPPP samples were studied in present work and their conformational and optical characteristics were obtained. The study has been accomplished using the unique combination of molecular hydrodynamics and optical methods. On the basis of hydrodynamic data the conclusions on conformational parameters were formulated. Furthermore, the conformational comparison of synthesized sample series was carried out.

Moreover computer simulation of HBPPP was carried out with HYDRO software and conformational parameters were calculated for two limiting cases (first, sphere and, second, rod model) [2]. The simulation results were found to be in good agreement with experimental data.

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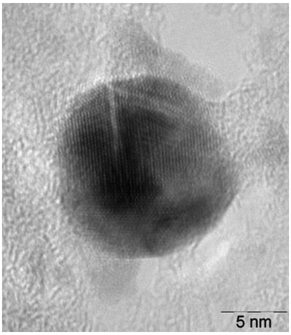
P-54

THE STUDY OF ARGENTUM NANOPARTICLES STABILIZED WITH MODIFIED PEG

N. V. Tsvetkov, A. A. Lezov, A. S. Gubarev, E. V. Ubyivovk,
N. V. Girbasova, A. Y. Bilibin

St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034, Russia
(a.gubarev@spbu.ru)



In recent decades the growing interest is demonstrated by multidisciplinary scientific groups in the study of nanoparticles (NPs) on the basis of noble metals (gold, silver, platinum). Former, this is explained by the intermediate position taken by these formations between the atomic-molecular level and the condensed matter state and latter, due to the fact that this NPs show unusual, interesting and useful properties [1, 2]. In particular systems containing noble metal NPs have broad prospects for their use as components for creating nanomaterials in microelectronics and optical devices, in obtaining of high performance and selective catalysts for the synthesis of new composite materials which are used in modern medicine, pharmacy, cosmetics and food industry.

In this study PEG was modified with end dendritic fragments containing amino groups. This modified PEG can act as a reductant and stabilizer of silver NPs. The investigation of the process of their formation, as well as the resulting system represents the important task. For resolving this problem the molecular hydrodynamic methods (dynamic light scattering, velocity sedimentation) and TEM have been used for both to study the components of the complexes and the resulting formation. The fact of NP formation has been established. Furthermore the dimensions of resulting NPs have been determined and compared within data of engaged methods. The satisfactory agreement of results was demonstrated.

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P-55

SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF POLYPYRROLE/TiO_2 AND POLYPYRROLE/ZnO COMPOSITES

L. Kratofil Krehula[a], S. Krehula[b], V. Gilja[a], A. Husak[a], M. Perlog[a],
J. Stjepanović[a], S. Šuka[a], Z. Hrnjak-Murgić[a]

[a]Faculty of Chemical Engineering and Technology, University of Zagreb,
Marulićev trg 19, HR-10000, Zagreb, Croatia
[b]Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180,
HR-10002 Zagreb, Croatia
(krehula@fkit.hr, www.fkit.hr)

Titanium dioxide (TiO_2) and zinc oxide (ZnO) can be used as photocatalysts for water purification. However, one particular interest is given on the integration of inorganic TiO_2 and ZnO nanoparticles with conducting polymers[1,2] because the resulting nanocomposites may possess unique properties and enhanced photocatalytic activity in comparison to pure TiO_2 and ZnO, using UV and also visible light. It is needed to explore the appropriate structure of polypyrrole that can induce activation of TiO_2 and ZnO photocatalyst since the synthesis of organic/inorganic hybrid materials can result in a synergistic and complementary feature, increasing TiO_2 and ZnO photocatalytic efficiency.

In this paper several different composites of polypyrrole/titanium dioxide and polypyrrole/zinc oxide (PPy/TiO_2 and PPy/ZnO composites) were studied. Composite samples were characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy and scanning electron microscopy (SEM). The photocatalytic efficiency of prepared composite samples was determined by following the decomposition of Reactive Red 45 (RR 45) dye under UV and visible light, which was monitored by UV-Vis spectroscopy (as a change in absorbance of characteristic wavelength at 542 nm). The obtained results showed good photocatalytic efficiency of nanocomposite samples under UV light. Some of the samples also showed excellent photocatalytic effect under visible light.

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P-56

SELF-ORGANIZATION PROCESSES IN LECITHIN-BILE SALT MIXTURES: COMPUTER SIMULATION

A. Markina[a], V. Ivanov[a], P. Komarov[b], A. Khokhlov[a], S.-H. Tung[c]

[a]*Moscow State University, Moscow, Russian Federation*
[b]*Institute of Organoelement Compounds RAS, Moscow, Russian Federation*
[c]*National Taiwan University, Taipei, Taiwan*

Problems of self-organization of biological surfactants have attracted increasing interest due to a wide range of practical applications. There are two main classes of surfactants: phospholipids and bile salts. Phospholipids, zwitterionic surfactants, typically form a bilayer or vesicles in aqua solutions and reverse micelles in organic solvents, such as hexane or cyclohexane, for example. Bile acids are also amphiphilic molecules, their main feature is facial morphology with polar and nonpolar surfaces [1].

We have performed computer simulation of three-component systems consisting of lecithin, bile salt and solvent, which may be water or an organic solvent, and studied the structure of molecular aggregates. We found that formation of "worm-like" micelles is observed in hexane-lecithin solution with increasing bile salt concentration (Fig. 1). Addition of bile salts into the aqueous lecithin solution also induces formation of elongated structures with ellipsoidal or cylindrical shape. Aggregates morphology in lecithin - bile salts mixture could be affected by inorganic salt. We believe that the formation of long flexible worm-like micelles can be the reason for the experimentally observed viscosity increase.

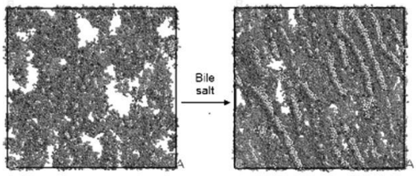

Fig.1. Structures formed in the hexane - lecithin solution by increasing bile salt concentration.

The authors acknowledge the financial support from RFBR (grant 14-03-92004-NNS, grant 16-33-00294 MOL_a) and MOST (Taiwan). We thank Moscow State University Supercomputer Center for providing the computational resources.

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P-57

COARSE-GRAINED COMPUTER SIMULATION OF CRYSTALLIZATION IN POLYIMIDE MELTS

A. Markina[a], V. Ivanov[a], P. Komarov[b], S. V. Larin[c], S. V. Lyulin[c]

[a]*Lomonosov Moscow State University, Moscow*
[b]*Tver State University, Tver*
[c]*Institute of Macromolecular Compounds, RAS, St. Petersburg*

Crystallization in polyimides melts plays a key role in their characteristics. The degree of crystallinity, depending on type of particular polyimide material, could either improve the mechanical properties (modulus increase) or lead to larger deterioration (increasing of brittleness). In this work we study behavior of two polyimides which are based on 1,3-bis-(3’,4-dicarboxyphenoxy)-benzene (dianhydride R) and various types of diamines:4,4’-bis-(4’’-aminophenoxy)-diphenylsulfone (diamine BAPS) and 4,4’-bis-(4’’-aminophenoxy)-diphenyl (diamine BAPB) [1]. The main structural difference of these polyimides is the presence of an additional SO_2 group in the R–BAPS diamine fragment compared to the R–BAPB one. This modification of the polymer chain leads to decrease of the persistence length, and as a result to increase of the flexibility of R-BAPS diamine fragment. We have developed and parameterized coarse-grained models for each of two types of the polyimides, semi-crystalline and amorphous one. All calculations have been carried out by means of dissipative particle dynamics simulations [2].

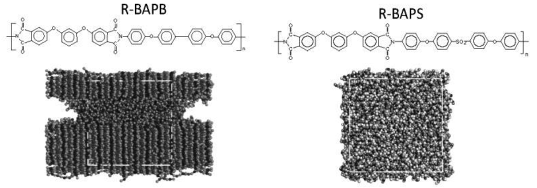

Fig. 1. Chemical structures of the repeating units (at the top) and morphologies (at the bottom) of thermoplastic heat-resistant polyimides R–BAPB (on the left) and R–BAPS (on the right).

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P-58

PREPARATION AND SELF-ASSEMBLY OF AMPHIPHILIC HYBRID POLYMER/GOLD NANOPARTICLES AT LIQUID-LIQUID INTERFACE

J. Tian, P. Vana

Institute of Physical Chemistry, Georg-August-University Göttingen,
Tammannstr. 6, D-37077 Göttingen, Germany
(jia.tian@chemie.uni-goettingen.de)

Amphiphilic hybrid gold nanoparticles (AuNPs) were prepared by liquid-liquid interface reaction between PS-SH in toluene and AuNPs in aqueous solution (Figure 1a). PS-Au NPs colloids were generated by the self-assembly of the amphiphilic hybrid AuNPs.[1] Flower-like core-shell hybrid particles were synthesized by combining the self-assembly of nanoparticles and polymer with a silica coating strategy (Figure 1b). The silica coating improves the thermal stability and dispersibility of the AuNPs. Also Fe_3O_4 nanoparticles were encapsulated in the core obtaining magnetic flower-like core-shell hybrid particles via the same strategy (Figure 1c).[2] These particles have potential applications in biomolecular separation, in high temperature catalysis, and as nanoreactors.

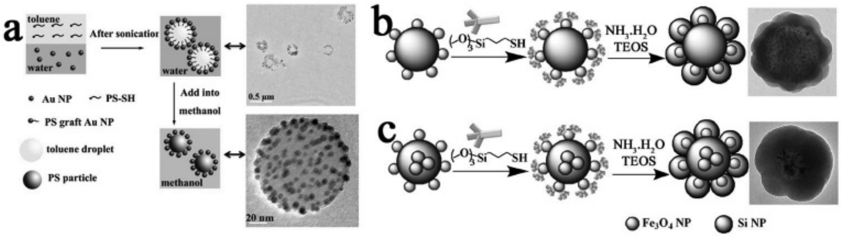

Figure 1. Schemes and TEM images for the Preparation of (a) Colloidal Particles with PS Cores and AuNPs Coronae, (b) core–shell hybrid particles with PS-AuNPs as the core and silica particles as the shell, (c) magnetic core–shell hybrid particleswith Fe_3O_4-PS-AuNPs as the core and silica particles as the shell.

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P-59

FORMATION OF SURFACE MODIFIED CORE/SHELL (Fe_3O_4@SiO_2) NANOPARTICLES OF CD(β-CYCLODEXTRIN) FOR DETECT AND SEPARATION OF DYES

S. E. Hong, K. J. Jang, K. R. Yoon

Chemistry Based Bio Hybrid Sensor Research Team(BK21 plus), Organic Nano Material Lab, Department of Chemistry, Hannam University, 1646 Yuseong-daero, Yuseong-gu, Daejeon, 305-811, KOREA

(kryoon@hnu.kr)

Introduction of CD(β-Cyclodextrin) to core/shell(Fe_3O_4@SiO_2) nanoparticles is a first step in their applications to sensors, catalysis, and nanotechnology in general. Magnetic nanoparticles were used for developing target specific magnetic resonance imaging (MRI) contrasts agents and bio-separation applications.[1] We reported surface modified core/shell(Fe_3O_4@SiO_2) nanoparticles of CD(β-Cyclodextrin) as one of our goals to introduce various functional groups onto surfaces. CD has been successful in introducing to core/shell(Fe_3O_4@SiO_2) nanoparticles surface and will contribute to the development of detect and separation system.[2] The resulting hybrid nanoparticles was confirmed by FE-SEM(Field-emission Scanning Electron Microscope), FE-TEM(Field-Emission Transmission Electron Microscope), EDS(Energy Dispersive X-ray Spectroscopy), FT-IR(Fourier Transform Infrared Spectroscopy), DLS(Dynamic Light Scattering), TGA(Thermogravimetric Analysis), ^{1}H-NMR(^{1}H Nuclear Magnetic Resonance) and ESI-MS(Electrospray Ionization-Mass Spectrometry).

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P-60

ANOTHER STEP TO ZERO BAND GAP PLASTICS: A SOLUBLE, LOW BAND GAP BISTHIADIAZOLE BASED ELECTROCHROMIC POLYMER

M. Icli Ozkut

Yuzuncu Yil University, Department of Chemical Engineering, 65080 Van, Turkey (mozkut@yyu.edu.tr)

A soluble and low band gap π-conjugated electrochromic polymer, poly(4,8-bis(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-5-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole) (**P1**), was electrochemically (**P1-E**) and chemically (**P1-C**) synthesized. Its electrochemical and optical properties were investigated. Cyclic voltammetry and UV-vis-NIR absorption measurements showed that **P1** has a narrow band gap ranging from 0.59 to 1.1 eV, depending on the band gap determination and synthesis (chemical or electrochemical) methods. **P1** demonstrated an ambipolar electrochemical behavior. The color of the polymer was gray in its neutral state and switched to green (first oxidation state) and blue (second oxidation state) upon oxidation and to brown upon reduction. There have been few studies on soluble and narrow band gap polymers in the literature, and only two studies of polymers having an extremely low band gap of about 0.5 eV have been published[1,2]. To the best of our knowledge, after these two polymers, **P1** is the soluble polymer with the lowest band gap recorded in the literature, with a band gap that varies from 0.59 to 1.1 eV.

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P-61

ACID/ BASE DOPED/ DEDOPED LOW BAND GAP POLYMER

G. Gokce[a], B. Karabay[b], A. Cihaner[b], M. Icli Ozkut[a]

[a]*Yuzuncu Yil University, Department of Chemical Engineering, 65080 Van, Turkey*

[b]*Atilim University, Chemical Engineering and Applied Chemistry, ATOMSEL, 06836 Ankara, Turkey*

(mozkut@yyu.edu.tr, http://atomsel.atilim.edu.tr/)

Polymer electrochromic based on thiadiazoloquinoxaline acceptor and 3,4-ethylenedioxythiophene donor, namely poly(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)-6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline) (PETQE), with a low band gap (0.57 eV) was synthesized and characterized. Electrochemical and optical studies showed that polymer film have both n- and p- type doping properties. Also, it is susceptible to nonoxidative/ nonreductive doping/ dedoping processes via lewis acid/ lewis base. As it known that among the conjugated polymers just polyaniline can be doped/dedoped via lewis acids/ bases. Recently Bendikov and his group published an article contains conjugated polymers having unsual nonoxidative doping process using lewis acids[1]. Since our polymer contains thiadiazole units like polymers of mentioned article, by inspiration of this precursor study we subjected our polymer to ammonia and hydrochloric acid, **P(ETQE)** responded both acid and base. By addition of ammonia **P(ETQE)** started to be dedoped and by addition of acid it started to doped. However, doping process of polymer is not totally finished like dedoping via base although high amount of acid added.

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P-62

SUCCESSIVE USE OF CYLINDER-FORMING DENDRON-JACKETED BLOCK COPOLYMERS AS TEMPLATES FOR SYNTHESIS OF NANOSTRUCTURED MESOPOROUS TiO_2/CARBON FILMS

W. T. Chuang[a], Y. M. Hsu[b], Y. S. Sun[b], U. S. Jeng[a]

[a]*National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan (weitsung@nsrrc.org.tw)*

[b]*Department of Chemical and Materials Engineering, National Central University, Taoyuan 32001, Taiwan*

We proposed a smart method to synthesize carbon-doped mesoporous TiO_2 films with controllable orientation of nanochannels using self-assembly thin films of dendron-jacketed block copolymers (DJBCP). The DJBCP is composed of amphiphilic dendrons (3Dn), selectively incorporated into the P4VP block of poly(styrene)-block-poly(4-vinylpyridine) (PS-b-P4VP) via hydrogen bonds. The PS-b-P4VP was used as structure-directing templates as well as the carbon source, whereas the supramolecular dendrons were designed for precisely guiding the titania precursors into P4VP domains of the films in addition to stabilize the cylindrical microdomains of DJBCP films. Using by grazing incident small-angle X-ray scattering (GISAXS), transmission electron microscope (TEM) and atomic force microscope (AFM), this work revealed that the formation of perpendicular cylinders resulted from the epitaxial growth from $Im\bar{3}m$ to P6mm via $R\bar{3}m$ in the DJBCP self-assembly films. The carbon-doped mesoporous TiO_2 films featured perpendicular and parallel nanochannels, and nanochannel/nanoparticle mesoporous bilayers were fabricated for promising applications including photovoltaics, catalysis, gas sensing, separation, and sustainable energy generation.

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P-63

EFFECT OF EPOXY STRUCTURES ON THERMAL CONDUCTIVITIES OF LIQUID CRYSTALLINE EPOXY/ALUMINA COMPOSITES

J. Kim, J. H. An, J. Y. Bae, D. J. Chung, S. H. Kim[a]

Dept. Polymer Sci. & Eng., Sungkyunkwan University, Suwon, Gyyeonggi 440-746, Korea, [a]Dept. Nano & Biotechnology, Gachon University, Seungnam, Korea

Various epoxies (two commercial epoxies, bisphenol A diglycidyl ether (DGEBA) and 3,3',5,5'-tetramethyl-4,4'-biphenol diglycidyl ether (TMBP), and a series of synthesized liquid crystalline epoxies (LCE), typically 4,4'-bis(4-hydroxybenzylidene)-diaminophenylene diglycidyl ether (LCE-DP) and other LCEs) and 4,4'-diaminodiphenylsulfone (DDS) were employed as a base epoxy resin and a curing agent, respectively, to investigate the effect of backbone structure of epoxy on the thermal conductivity of epoxy/alumina composite. Alumina (Al_2O_3) of commercial source was applied as an inorganic filler. The DGEBA structure has an amorphous state and the TMBP structure shows a crystal phase. On the other hand, LCE-DP structure exhibits a liquid crystalline phase. The curing behaviors and thermal conductivities are very dependent on the molecular structure of epoxies. The heat of curing of epoxy resin was measured with dynamic differential scanning calorimetry (DSC). Thermal conductivity was measured by a laser flash method and the experimental values are compared with values predicted by theoretical models. It was found that the thermal conductivity of the LCE-DP structure was higher than that of the commercial epoxy such as TMBP and DGEBA and the experimental data fits well with values predicted theoretically.

P-64

COMBUSTION CHARACTERISTICS OF FLAME RETARDANTS BASED ON POLY(PHOSPHORIC ACID ESTER)

J.-H. Ye, S.-H. Choi*

Department of Chemistry, Hannam University, 1646 Yuseong-daero,
Yuseong-gu, Daejeon, 34054, Korea
**(shchoi@hnu.kr)*

Non-halogen flame retardant polymer materials are in the grate demand for manufacturing printed circuit boards in electrical and electronic equipment because recently the use of halogen flame retardants in plastic materials has raised many questions about their impact on the health and safety of both and environment.[1,2] In recent years, significant attention has focused on the research on active phosphorus-containing flame retardant, nanofiller and their synergetic effects.

In the study, for applying flame retartant fillers to polymer composite, we synthesized the poly(phosphoric acid ester), and characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Nuclear Magnetic resonance spectroscopy (NMR), Thermogravimetric Analysis (TGA), Scanning electron microscopy (SEM), gas chromatograph-mass spectrometer(GC-MS) and Limiting oxygen index Test (LOI test) for the synthesized flame-retardants. The application of the preparing the fire-retardant polymer materials is in progress.

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P-65

BIODEGRADABLE NANOCONTAINERS COMPOSED OF ANIONIC LIPOSOMES AND CATIONIC POLYPEPTIDE VESICLES

A.V. Sybachin[a], O.V. Zaborova[a,b], T.J. Deming[c], A.A. Yaroslavov[a]

[a]*Chemistry Department, M.V. Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow, 119991, Russian Federation (sybatchin@mail.ru)*

[b]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*

[c]*Department of Bioengineering, University of California, Los Angeles, CA 90095, USA*

Spherical lipid bilayer 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. We suggest electrostatic assembly of liposomes, composed of anionic palmitoyloleoyl phosphatidylserine (POPS) and zwitterionic dioleoylphophatidylcholine (DOPC), with bilayered vesicles composed of cationic poly(L-lysine)-b-poly(L-leucine) block copolypeptides for concentration of liposomes within a small volume. This approach allows one to create multiliposomal carriers filled with different substances at desirable content ratios.

We demonstrate how to manipulate with number of liposomes that could be ultimately adsorbed on polypeptide vesicles and the stability of the complexes in water-salt media by varying of POPS fraction in the liposomal membrane. The complexes were found to have low cytotoxicity. Also polypeptide vesicles and their complexes with liposomes are effectively digested by proteolytic enzyme trypsin.

The effectiveness of interaction of the complexes with cell membranes was shown by fluorescence microscopy.

These findings as well as the high potential for loading of anionic liposomes and cationic vesicles with biologically active compounds make these multi-liposomal complexes promising in the drug delivery field.

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

P-66

EFFECT OF SOLVENT QUALITY ON THE CHROMATOGRAPHIC SEPARATION OF LINEAR AND H-SHAPED POLYMERS: A MONTE CARLO STUDY

X. Wang[a], Z. Limpouchová[a], M. Lísal[b,c], K. Procházka[a]

[a]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 00 Praha 2, Czech Republic*

[b]*Laboratory of Chemistry and Physics of Aerosols, Institute of Chemical Process Fundamentals of the CAS, v. v. i., Rozvojová 135/1, 165 02 Prague 6-Suchdol, Czech Republic*

[c]*Department of Physics, Faculty of Science, J. E. Purkinje University, České Mládeže 8, 400 96 Ústí n. Lab., Czech Republic*

The partitioning of linear and H-shaped polymers between bulk solvent and narrow pores with inert and attractive walls was studied by Monte Carlo method described in our recent publication[1]. Here, we focus on the effect of solvent quality and polymer concentration on the partitioning. We study the pore-bulk equilibria in systems that are relevant to chromatographic experiments. It means that the pore sizes are comparable with the polymer chain size and polymer concentrations are very low (volume fraction ca. 0.02). In agreement with other authors[2], we found that the partition coefficients depend strongly on both solvent quality and concentration. The dependences can be explained on the basis of thermodynamic considerations as the interplay of osmotic pressure and geometric confinement. With decreasing solvent quality, the osmotic pressure decreases because polymer coils are smaller. The analysis of the scaling behavior of polymer chains in both bulk and pore shows that the "effective solvent quality" is deteriorating with increasing confinement effect. In summary, the simulations show that in the region of low concentration relevant to chromatography, the partition coefficient increases in good solvent with concentration and decreases in θ solvent.

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P-67

INFLUENCE OF CORONA STRUCTURE ON BINDING OF AN IONIC SURFACTANT IN OPPOSITELY CHANGED AMPHIPHILIC POLYELECTROLYTE MICELLES

F. Delisavva[a], M. Uchman[a], J. Skvarla[a], E. Wozniak[b], E. Pavlova[c], M. Slouf[c], V. Garamus[d], K. Prochazka[a], M. Stepanek[a]

[a]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 12840 Prague 2, Czech Republic*
[b]*Department of Chemistry, The Faculty of Food Science, Wrocław University of Environmental and Life Sciences, 50-375 Wrocław, C. K. Norwida 25, Poland*
[c]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*

[d]*Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, D-21502 Geesthacht, Germany*

Interaction of polystyrene-*block*-poly(methacrylic acid) micelles (PS-PMAA) with cationic surfactant N-dodecylpyridinium chloride (DPCl) in alkaline aqueous solutions was studied by static and dynamic light scattering, SAXS, cryogenic transmission electron microscopy, isothermal titration calorimetry and time-resolved fluorescence spectroscopy. It has been discovered that there are two distinct regimes of surfactant binding in the micellar corona by different interaction of DPCl with PMAA in the inner and outer parts of the corona. The compensation of the negative charge of the micellar corona by DPCl leads to the aggregation of micelles and the micelles form colloidal aggregates at a certain critical surfactant concentration. The aggregates are formed by individual micelles with intact cores and collapsed coronas interconnected with surfactant micelles by electrostatic interactions. Unlike polyelectrolyte-surfactant complexes formed by free polyelectrolyte chains[1-3], the PMAA/DPCl complex with collapsed corona does not contain surfactant micelles.

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P-68

ENVIRONMENTALLY FRIENDLY SUPERABSORBENT POLYMERS FOR WATER-HOLDING IN AGRICULTURAL LANDS AND THEIR APPLICATION FOR ENVIRONMENTAL PURPOSES

T. Erşen Dudu, D. Alpaslan, N. Aktaş

Department of Chemical Engineering, Faculty of Engineering and Architecture, Yuzuncu Yil University, Van, Turkey

(naktas@gmail.com)

Hydrogels are three-dimensional crosslinked polymeric networks and receiving great interest due to their promising applications such as sensors, separation membranes, absorbents, and materials in medicine and pharmacy as drug delivery systems, in solving some ecological and biological problems as well as in modern technologies. These hydrogels are generally known as superabsorbent that they can absorb large amounts of water, as much as hundreds of times their own mass[1-2]. In the present study, p(DMAAm) hydrogel was synthesized by using N,N-Dimethylacrylamide (DMAAm) as monomers and modified by hydrochloric acid (HCl) for targeted nitrogen fertilizer removal. p(DMAAm)-HCl hydrogel was investigated swelling behaviors in deionize water and sensibility pH and were characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and Thermal Gravimetric Analysis (TGA). In the environmental applications of p(DMAAm) hydrogel aimed removal from aqueous medium of nitrogen fertilizer (urea and ammonium nitrate). Therefore in this study investigated effect on the absorption performance of initial fertilizer concentration (mg/L), the pH of the media, and temperature (°C). Ultra-Viole spectroscopy was used to quantify nitrogen fertilizer during absorption studies. The most utilized absorption isotherms models like Langmuir and Freundlich were studied to obtain the best-fitted isotherms equation. Moreover thermodynamic parameters were evaluated. Under specified experimental conditions, the maximum absorption capacities for nitrogen fertilizer were calculated to be approximately 160 mg/g.

Keywords: N,N-Dimethylacrylamide, urea, ammonium nitrate, modification

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P-69

SYNTHESIS, CHARACTERIZATION AND POSSIBLE AGRICULTURAL APPLICATION OF NONIONIC p(DMAAm) HYDROGEL

T. Erşen Dudu, D. Alpaslan, N. Aktaş

Department of Chemical Engineering, Faculty of Engineering and Architecture, Yuzuncu Yil University, Van, Turkey
(tuba_ersen@hotmail.com)

With the development of technological science, the demands on new polymeric materials are increasing rapidly. Superabsorbent or water retaining material is considered as one of the promising materials that are widely used in industrial and agricultural fields. They are natural or synthetic materials that can absorb large amounts of water, as much as hundreds of times their own mass [1-2]. In this investigation nonionic p(DMAAm) hydrogel was synthesized by using N,N-Dimethylacrylamide (DMAAm) as monomers and utilized for targeted nitrogen fertilizer removal. Synthesized nonionic p(DMAAm) hydrogel was investigated swelling behaviors in deionize water and sensibility pH and were characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and Thermal Gravimetric Analysis (TGA). In the environmental applications of nonionic p(DMAAm) hydrogel aimed removal from aqueous medium of nitrogen fertilizer. Therefore in this study investigated effect on the absorption performance of initial fertilizer concentration (mg/L), the pH of the media, and temperature (°C). Ultra-Viole spectroscopy was used to quantify nitrogen fertilizer during absorption studies. The most utilized absorption isotherms models like Langmuir and Freundlich were studied to obtain the best-fitted isotherms equation. Moreover thermodynamic parameters were evaluated. Under specified experimental conditions, the maximum absorption capacities for nitrogen fertilizer were calculated to be approximately 120 mg/g.

Keywords: N,N-Dimethylacrylamide, nitrogen fertilizer, absorption

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P-70

CHARACTERIZATION OF CATIONIC HYDROGELS AND THEIR REMOVAL OF PHENOL RED TEXTILE DYES FROM AQUEOUS ENVIRONMENT

T. Erşen Dudu, D. Alpaslan, N. Aktaş

Department of Chemical Engineering, Faculty of Engineering and Architecture, Yuzuncu Yil University, Van, Turkey (alpaslanduygu@gmail.com)

Pollutants from industries such as textile, printing, plastic, food, paper, pharmaceutical, cosmetic and leather tanning are rather rich in dye and they are non-biodegradable, complex organic molecules and even carcinogenic. Therefore, the discharges to the nearest specially water sources of these pollutants causes of environmental pollution as water and soil. Because, ın recent years, there are many studies focused on removal of textile dyes form contaminant aqueous environments [1-2]. In this study, cationic p(DMAAm-co-APTMACl) hydrogels were synthesized at different molar ratios using N,N-Dimethylacrylamide (DMAAm) and 3-acrlylamidopropil-trimethyl ammonium chloride (APTMACl) based the monomers. Fourier Transform Infrared Spectroscopy (FT-IR) and Thermal Gravimetric Analysis (TGA) techniques were utilized for the synthesized hydrogels characterization. Ultra-Viole spectroscopy was used to quantify phenol red during absorption studies. The swelling behaviors, pH sensitivity of the synthesized hydrogels were also studied. In the environmental applications of synthesized hydrogels aimed removal from aqueous medium of textile dye such as phenol red. Therefore, in this study investigated effect on the absorption performance of initial dye concentration, the pH of the media, different gels ratio and contact time. Moreover the applicability of the Langmuir and Freundlich isotherms for the absorption present dye was investigated at different dye concentration.

Keywords: Hydrogels, Phenol red, N,N-Dimethylacrylamide, 3-acrlylamidopropil-trimethyl ammonium chloride

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P-71

DECORATION OF DNA SCAFFOLD BY GOLD NANOPARTICLES FORMED IN AQUEOUS SOLUTIONS

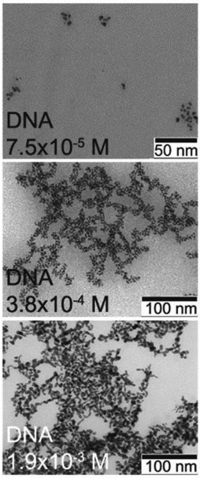
E. Karpushkin, L. Lopatina, V. Sergeyev

Chemistry Department, Moscow State University, Leninskie Gory 1-3,
Moscow, 119991, Russia
(eukarr@gmail.com)

The high affinity of DNA to transition metals has been utilized to template various nanostructures applicable in nanoelectronics, catalysis, sensors production, etc[1]. In order to better understand the formation of such complex structures, we studied the influence of DNA macromolecular template on the gold nanoparticles (GNP) formation via reduction with sodium borohydride.

Reduction of 3.8×10^{-4} M. $HAuCl_4$ by $NaBH_4$ in the presence DNA (at the molar ratio of 1:1:1 or 1:10:1 with respect to the nucleotides amount) produced ~3 nm GNP. At the equimolar amount of the reducing agent, isolated nanoparticles were formed, whereas in the excess of $NaBH_4$ they were assembled along the linear template (DNA macromolecules).

To clarify the effect of the template amount on the morphology of gold nanostructures, we performed the $HAuCl_4$ reduction at the 1:10:1 molar ratio of the reactants varying the DNA concentration. TEM images of the products are shown in the Figure.



In conclusion, we have demonstrated that DNA molecule templates one-dimensional nanostructures in reducing aqueous solutions of $HAuCl_4$, with DNA being either decorated by a large number of small 3 nm gold nanoparticles or by continuous gold nanoribbons. The formation of such assembles is strongly dependent on the concentration of DNA template.

This work was supported by RFBR (project 14-03-00696_a).

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P-72

FLUORESCENCE LIFETIME IMAGING OF POLYMER THERAPEUTICS

J. Pánek, E. Koziolová, P. Štěpánek, T. Etrych, O. Janoušková

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(panek@imc.cas.cz, www.imc.cas.cz)

Macromolecular and supramolecular carriers with bound or incorporated drugs, e.g. soluble polymers, micelles, polymer-coated liposomes and nanoparticles, have attracted special attention for significant improvements in delivery of anticancer therapeutics. Due to intrinsic fluorescence of certain therapeutics, biological interactions of their nano-formulations can be followed by advanced fluorescence detection methods: fluorescence lifetime imaging microscopy (FLIM) and fluorescence lifetime correlation spectroscopy (FLCS).[1,2] In our contribution we describe FLIM data processing technique called pattern decomposition[3] applied to follow distributions of physicochemical states of anthracycline drugs doxorubicin and pirarubicin and their conjugates with poly[N-(2-hydroxypropyl)methacrylamide] (pHPMA) within living cells. The pattern decomposition calculations confirm not only the ability of the technique to find free and bound anthracycline drug in the FLIM image, but also to distinguish between patterns of originally free drug added to the cells and drug released from conjugate with the polymer.

The work was supported by the Ministry of Education, Youth and Sports of CR within the National Sustainability Program I (NPU I), Project POLYMAT LO1507.

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P-73

DUAL-RESPONSIVE INJECTABLE POLYMER DEPOTS VISUALIZABLE BY ^{19}F-MRI

O. Sedláček[a], D. Jirák[b], A. Galisová[b], M. Hrubý[a]

[a]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(sedlacek@imc.cas.cz, www.imc.cas.cz)
[b]MR Unit, Department of Diagnostic and Interventional Radiology,
Institute for Clinical and Experimental Medicine,
Vídeňská 1958/9, 140 21 Prague, Czech Republic

Fluorine ^{19}F magnetic resonance imaging (MRI) represents a promising tool for experimental and diagnostic imaging due to its high specificity caused by negligible abundance of fluorine in living tissues. Here we present a novel dual-responsive system for ^{19}F MRI visualization of injectable polymer depots. The main matrix consists of poly[*N*-(2,2-difluoroethyl)acrylamide-*co*-*N*-(3-imidazolylpropyl)acrylamide], which is sensitive to both temperature and pH. With decreasing pH, the cloud point temperature rises, as the protonation of imidazole groups occur. The relaxometry showed relaxivity dependence on temperature, both relaxivity r_1 and r_2 were lower with increasing temperature. Temperature-varied MRI experiment confirmed that dependence; we observed markedly lower MR signal in the phantoms with increasing temperature. The minimal concentration of the agent detected within reasonable measurement time for *in vivo* experiments (34 min) was 18 mM of fluorine. In the *in vivo* measurement, the polymer was injected into the muscle (right hind leg) and into the subcutaneous area of brown Norway male rats. Strong ^{19}F MR signal was detected at both injection sites; the highest signal was detected 2 hours after polymer administration.

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P-74

POLYMER NANOPARTICLES WITH REACTIVE OXYGEN SPECIES (ROS)-TRIGGERED CARGO RELEASE FOR DRUG DELIVERY APPLICATIONS

E. Jäger, A. Höcherl, A. Jäger, M. Hrubý, O. Janoušková, R. Konefał,
M. Netopilík, J. Pánek, M. Šlouf, K. Ulbrich, P. Štěpánek

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

(jager@imc.cas.cz; www.imc.cas.cz)

New drug-delivery systems of polymer nanoparticles (NPs) bearing pinacol-type boronic ester and alkyne moieties (Fig. 1a) or bearing oxalate based moieties (Fig. 1b) that displays triggered self-immolative polymer degradation in the presence of reactive oxygen species (ROS) with the capability of cellular imaging are presented. The NPs specifically release their drug cargo under concentrations of ROS that are commonly found in the intracellular environment of certain tumors and of inflamed tissues (Fig. 1c) and exhibit significant cytotoxicity to cancer cells (Fig. 1d) compared to their non-ROS-responsive counterparts.

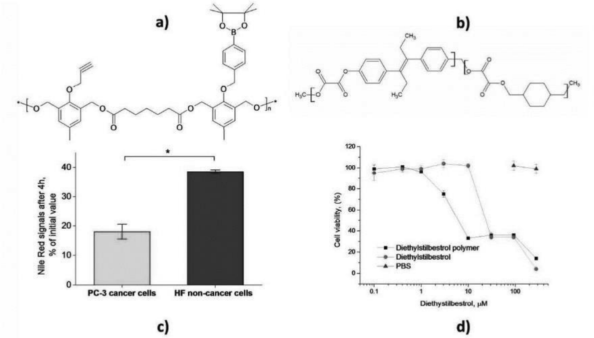

Figure 1. Polymer structures of the pinacol-type boronic ester (NP1) (a) and the oxalate based moieties (NP2) (b). The higher Nile Red (NR) release from NR-loaded ROS responsive NP1 in PC-3 (cancer) in comparison with HF (non cancer) cells after 4 h of incubation demonstrating the specificity of the NPs to ROS rich environments (c) and the higher citotoxicity of the NP2 in PC-3 cells when compared with the free drug, diethylstilbestrol (d).

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P-75

PEGYLATED POLYESTER NANOPARTICLES FOR DELIVERY OF PACLITAXEL: SYNTHESIS, CHARACTERIZATION AND *IN VITRO* STUDIES

A. Jäger[a], E. Jäger[a], M. Hrubý[a], R. Konefał[a], Z. Syrová[b], T. Mazel[b],
D. Cmarko[b], I. Raška[b], P. Štěpánek[a]

[a]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
[b]Institute of Cellular Biology and Pathology, 1st Faculty of Medicine, Charles University in Prague, Albertov 4, 128 01 Prague 2, Czech Republic (ajager@imc.cas.cz)

Polyester-based nanostructures are widely studied in drug delivery systems due to nanoscale-related effects, biocompatibility and biodegradability. In this work we describe such biodegradable and biocompatible system for the delivery of the anticancer drug paclitaxel (PTX). PTX-loaded polymer nanoparticles based on poly(ethylene glycol) methyl ether-*b*-poly(propylene succinate)-*b*-poly(ethylene glycol) methyl ether (mPEG-PPS-mPEG) with different particle sizes (30, 70 and 150 nm) were prepared and their release rate, enzymatic degradation, particles size stability in complex media and cytotoxicity to cancer cells were analyzed in *in vitro* studies. The results indicate that PTX is faster released from the biggest particles (70 and 150 nm) in phosphate buffer saline (PBS, pH 7.4) where ~ 70% of the drug is released in 120 hours in comparison to ~ 50 % from the particles with 30 nm. The *in vitro* enzymatic degradation experiments in presence of the enzyme Lipase from porcine pancreas demonstrated that the particles degradation is size dependent and the complete degradation occurs in less than ~ 48 h for all particles sizes. The *in vitro* cytotoxicity studies on HeLa cells showed an important increase in the cytotoxicity of the PTX-loaded particles in comparison with the free PTX. Finally, particles sizes stability experiments (dynamic light scattering) performed in diluted blood plasma (5 % plasma diluted in PBS) with the 30 nm particle sizes indicates that they are suitable for *in vivo* applications in cancer chemotherapy.

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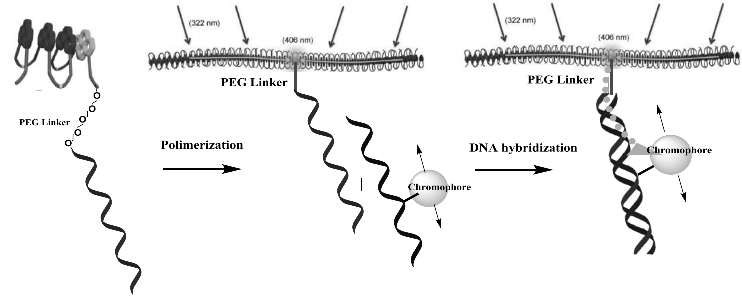
P-76

EFFICIENT LIGHT-HARVESTING ANTENNA THROUGH THE INTERMEDIATE DONOR-ACCEPTOR PYRENE DERIVATIVE

M. Kownacki, S. M. Langenegger, R. Häner

Department of Chemistry and Biochemistry, University of Bern,
Freiestrasse 3, CH-3012 Bern, Switzerland
(mariusz.kownacki@dcb.unibe.ch)

Efficient artificial light-harvesting antennas composed of multichromophoric array in a DNA scaffold are nowadays a key aspect in the supramolecular photochemistry [1]. Recently it was reported that the phenanthrene-pyrene supramolecular polymers can efficiently absorb photons which are transferred to the pyrene collection centre [2]. To expand this idea, 3,6-dialkynylphenanthrene trimer and new pyrene related oligomers were synthesized. As the DNA scaffolds are ideal platforms to organize chromophores the interesting point due to energy transfer is to introduce another acceptors in well-defined interchromophore distance from pyrene. This approach can be done by introducing complementary strand which contains appropriate chromophore in different position. Such a supramolecular complexes were investigated with different spectroscopic methods to prove efficient harvesting and transport of energy to the acceptor core through the intermediate donor-acceptor pyrene derivative.



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P-77

CONTROLING MEMBRANE STRUCTURE OF HYBRID POLYMER/LIPID GIANT UNILAMELLAR VESICLES

T.P.T. Dao[a,b], F. Fernandes[b], K. Ferji[a], M. Prieto[b],O. Sandre[a],
J. F. Le Meins[a]

[a]*LCPO, Univ. of Bordeaux / CNRS UMR 5629, 33600 Pessac, France*
[b]*CQFM INN, Universidade de Lisboa, 1049-001 Lisboa, Portugal*
(lemeins@enscbp.fr)

Microdomains formation in hybrid polymer/lipid giant unilamellar vesicles (GHVs) has been described over the last few years (1,2). GHVs can be viewed as advanced vesicular structures since compared to their liposome and polymersome forerunners, they potentially marry in a single membrane the best characteristics of the two separate components. Here, we aim to map a global picture of phase separation within giant hybrid vesicles by using various copolymer based on Poly(dimethylsiloxane) and Poly(ethylene glycol) with different architectures (grafted, triblock) and molar masses allowing to tune membrane thickness, combined with lipid in a fluid (POPC) or gel state (DPPC) at room temperature. Thanks to confocal imaging and advanced Fluorescence Microscopy techniques (FLIM, FRAP), we demonstrate that in addition to the lipid/polymer fraction or lipid physical state, the line tension at the lipid polymer/lipid boundaries modulated by the molar mass of the copolymer used and membrane tension modulated either by osmotic shock or micropipettes succion are the most important factors involved in formation of stable lipid domains of different size and morphologies in GHVs.

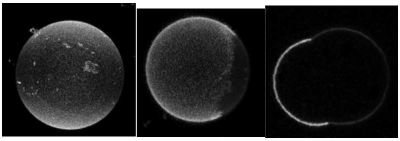

Figure. Different morphologies of GHV obtained by playing on line tension or membrane tension.

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P-78

TOWARDS THE CONTROL OF NANODOMAIN FORMATION IN LARGE HYBRID POLYMER/LIPID UNILAMELLAR VESICLES (LHV)

T.P.T. Dao[a,b], F. Fernandes[b], K. Ferji[a], M. M. Er-Rafik[c], M. Schmutz[c],
M. Prieto[b], O. Sandre[a], J. F. Le Meins[a]

[a]LCPO, Univ. of Bordeaux / CNRS UMR 5629, 33600 Pessac, France
[b]CQFM INN, Universidade de Lisboa, 1049-001 Lisboa, Portugal
[c]University of Strasbourg, ICS UPR 22 CNRS, 23 rue du Loess, 67034
Strasbourg, France
(lemeins@enscbp.fr)

Polymersomes, based on the self-assembly of amphiphilic block copolymers, have been viewed as potential formulation for multiple applications in nanomedicine field. Over the last few years, Hybrid Polymer/lipid Vesicles became even more attractive structures since they can associate the benefits of polymersomes (stability, chemical versatility) with the benefits of liposomes (biofunctionality, biocompatibility) (1). However, the control of their properties which is obviously linked to their structuration (domain formation via phase separation) is still far from being understood up to now, particularly at nanoscale (2). Here, by using various block copolymers based on poly(dimethylsiloxane) and poly(ethylene glycol) with different molar masses allowing to tune membrane thickness, combined with DPPC, a lipid gel state at room temperature, we have analysed Large Unilamellar Hybrid Vesicles (LHV) through different techniques. Small Angle Neutron Scattering (SANS) and contrast variation technique, which offer the unique possibility to study the structure of these complex mixtures at nanometric scales, Time-Resolved Förster resonance energy transfer (TR-FRET) and cryo-transmission electron microscopy (Cryo-TEM). We first show that hybrid lipid/polymer vesicles can present multiple small lipid domains of a few nanometers by fitting data with holey shell form factor and more generally that one of the important parameters governing the membrane structuration and the obtention of hybrid vesicle is the hydrophobic mismatch at the polymer/lipid boundaries.

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P-79

CONTROLLABLE SELF-ASSEMBLY OF BLOCK COPOLYMERS IN AQUEOUS SOLUTION: A SMALL ANGLE SCATTERING STUDY

T.-H. Kim[a], E. Kim[a], C. Do[b], H. Ahn[c], Y.-S. Han[a]

[a]*Neutron Science Division, Korea Atomic Energy Research Institute, 1045 Daedeock-daero, Yuseong-gu, Daejeon, 305-353, Republic of Korea*

[b]*Spallation Neutron Source, Oak Ridge National Laboratory, TN, USA*

[c]*Beam Line Division, Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang, Gyeongbuk 790-784, Republic of Korea*

(taehwan@kaeri.re.kr)

With a control in the external conditions such as temperature, additive or pH, block copolymers possessing both hydrophilic and hydrophobic moieties exhibit fascinating phase behaviors in aqueous solution, which can provide a broad spectrum of potential applications in nano- and biotechnology. Particularly, the Pluronic triblock copolymer (PEO_m-PPO_n-PEO_m), one of the typical amphiphilic block copolymers is highly biocompatible, and thus it is easily applicable for the practical use as biological materials. However, the phase behaviors of the Pluronic block copolymers have not been fully exploited yet under a variety of the external conditions, which provides key information for the practical application of block copolymers. Therefore, we have studied on the phase behavior of Pluronic block copolymers using in-situ small angle neutron and X-ray scattering. In this report, we will present a variety of self-assembled nanostructures of Pluronic triblock copolymers with different molecular weight in aqueous solution depending on temperature and additives [1-2].

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P-80

CHIRAL SEPARATION OF D,L -METOPROLOL THROUGH CELLULOSE MIXED MEMBRANES

P. Ai, H. Y. Xion

Department of Chemistry, Yunnan Normal University, Kunming, People's Republic of China

This work reports the chiral separation of D,L -metoprolol with cellulose mixed membranes. Cellulose derivatives were chosen as membrane material because they possesses multichiral carbon atoms in their molecular structure unit. A polymeric enantioselective mixed membrane was prepared by mix between microcrystalline cellulose and cellulose tris (3,5-dimethyl-phenyl-amino-methyl ester). The permselective properties of the mixed membrane was studied using a non-aqueous solution of D,L-metoprolol as the feed solution. The influences of some parameters, such as the mixed ratio of two Cellulose derivatives, the air-drying time of the membrane, the time of polymerization, the kinds of solution of D,L-metoprolol and the feed concentration of the D,L-metoprolol , were studied. The top surface and cross-section morphology of the resulting membrane were examined by scanning electron microscopy. When the membrane was prepared with 83.3 wt % microcrystalline cellulose and 16.7 wt % cellulose tris (3,5-dimethyl-phenyl-amino-methyl ester) in the DMA casting solution, and the solution of D,L-metoprolol and feed concentration of D,L-metoprolol were mixture of n-hexane/isopropanol/triethylamine(90:10:0.2, v/v/v) and 0.5 mg/mL, respectively, over 42.4% of enantiomeric excess could be obtained. The results showed that the cellulose mixed membrane can separate partly the optical isomers of D,L -metoprolol.

Keywords: enantioselective polymeric membrane; chiral separation; D,L-metoprolol; cellulose tris (3,5-dimethyl-phenyl-amino-methyl ester)

P-81

SELF-ASSEMBLED MICELLES OF POLY(VINYL ACETATE) -*B*-POLY(*N*-VINYL CAPROLACTUM） FOR TEMPERATURE-TRIGGERED DRUG DELIVERY

Y. M. Bi, P. L. Xu, G. Tang, F. X. He, D. You, F. Lin

College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, P.R. China
(yunmeibi@hotmail.com)

Amphiphilic poly(vinyl acetate)-*b*-poly(N-vinylcaprolactam) (PVAc-*b*-PNVCL) copolymers were synthesized by sequential reversible addition-fragmentation chain transfer (RAFT)/macromolecular design via the interchange of xanthates (MADIX) process. The copolymers are able to self-assembled into nanospherical micelles in the aqueous solution as revealed by fluorescent spectroscopy, transmission electron microscope (TEM) (Fig. 1) and dynamic light scattering (DLS). These micelles are temperature dependent due to the presence of thermoresponsive PNVCL blocks. The potential of these micelles to be used as smart drug delivery systems (DDS) is then investigated using breviscapine as a model drug. *In vitro* release tests show a desired thermoresponsive drug-release behavior (Fig. 2). The reversible and sensitive thermoresponse of these micelles might provide potential opportunities for a variety of biomedical applications.

Acknowledgements

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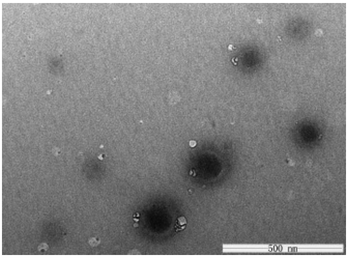

Fig. 1 TEM image of the formed micelles by PVAc-*b*-PNVCL.

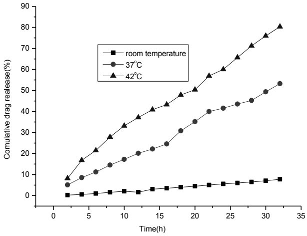

Fig. 2 *In vitro* release profile of breviscapine from PVAc-*b*-PNVCL micelles at 25, 37 and 42°C.

P-82

HOST–GUEST SUPRAMOLECULAR SYSTEM OF RZK ANTI-HIV AGENT AND β-CYCLODEXTRIN

C. Yuan, Q. Ruan, S. M. Chi, P. Zheng, Y. Zhao

College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650092, China
(zhaooyann@163.com)

Non-nucleoside reverse transcriptase inhibitors (NNRTIs) are a class antiretroviral drugs which play an important role in treatment of HIV-1 infection. Dihydro-alkoxy-benzyl-oxopyrimidines (DABOs) were one of the most representative classes of NNRTIs developed in the past decade. The DABOs derivatives RZK is characterized by good effect and low toxicity[1]. Unfortunately, RZK often present a poor bioavailability mainly due to low water solubility. Thus, it is difficult for RZK to be used as oral medications. Cyclodextrins (CDs) have a hydrophobic central cavity and a hydrophilic outer surface and can encapsulate various inorganic/organic molecules to form host–guest complexes or supramolecular species[2]. This usually enhances drug solubility in aqueous solutions and affects the chemical characteristics of the encapsulated drug in the pharmaceutical industry. The inclusion complexation behavior of RZK with β-CD was investigated in both solution and the solid state by means of NMR, XRD, SEM, IR spectroscopy. Furthermore, preliminary *in vitro* cytotoxicity assy showed that the complexes still maintain anti HIV-1 activities. The results showed that the water solubility and stability of RZK were obviously increased in the inclusion complex with β-CD.

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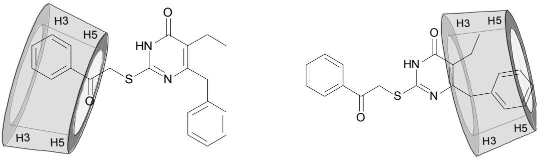

Figure Possible binding mode of the β-CD /RZK complex

P-83

COMPARISON OF STEROID- AND ALKYL-BASED DENDRITIC AMPHIPHILES FOR DRUG ENCAPSULATION

S. Ehrmann, B. N. S. Thota, R. Haag
Institute for Chemistry and Biochemistry, Freie Universität Berlin,
Takustr. 3, 14195 Berlin
(svenja.ehrmann@fu-berlin.de, www.polytree.de)

During the last decades, modern drug development and high-throughput screening approaches led to the discovery of drugs, which are low in molecular weight, hydrophobic and therefore poorly soluble in water. Thus, a low bioavailability is the consequence.

In this work, we investigate the encapsulation of hydrophobic drugs into stable supramolecular nanomicelles and demonstrate high encapsulation efficiencies of up to 20 wt-%. Our dendritic structures are steroid-based amphiphiles with polar glycerol-based dendritic headgroups, as well as amphiphiles with alkyl-based tails. The aggregation of these structures in water was investigated through surface tension and pyrene fluorescence measurements. Furthermore, we performed Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM) measurements for size and shape analysis. Finally, all compounds were analysed with respect to their cell compatibility using MTT and RTCA assays. We could demonstrate that all compounds showed no cytotoxic effects at low concentrations.

Encapsulation capacities with the anti-inflammatory drug Dexamethasone were determined for different amphiphile concentrations, as well as possible cooperative effects investigated regarding the interaction of steroidal structures. Our results demonstrate that all tested amphiphiles increase the water-solubility of Dexamethasone significantly.

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P-84

EFFECT OF pDADMAc CONCENTRATION ON ELECTROMECHANICAL PERFORMANCE OF CHITOSAN-BASED ELECTROACTIVE ACTUATORS

E. Altınkaya[a,b], Y. Seki[a], B. O. Gürses[c], Ö. C. Yılmaz[d], M. Sarıkanat[c], L. Çetin[e], O. Özdemir[f], İ. Şen[g], K. Sever[g]

[a]Dokuz Eylul University, The Graduate School of Natural and Applied Sciences, İzmir, Turkey
[b]Çanakkale Onsekiz Mart University, Faculty of Bioengineering, Çanakkale, Turkey
[c]Ege University, Department of Mechanical Engineering, İzmir, Turkey
[d]Dokuz Eylul University, Department of Mechatronics Engineering, The Graduate School of Natural and Applied Sciences, İzmir, Turkey

[e]Izmir Katip Celebi University, Department of Mechatronics Engineering, İzmir, Turkey
[f]Dokuz Eylul University, Department of Mechanical Engineering, İzmir, Turkey
[g]İzmir Katip Çelebi University, Department of Mechanical Engineering, İzmir, Turkey

emineakar@yandex.com, yoldas.seki@deu.edu.tr, ozguncemyilmaz@gmail.com, lvnt.cetin@gmail.com, okan.ozdemirr@hotmail.com, ibrahimsen.87@hotmail.com, kutlaysever@gmail.com, ouz.gurses@gmail.com

A novel chitosan-based electroactive actuator was fabricated by using chitosan, poly(diallyldimethylammonium) chloride (pDADMAc), N,N'-methylenebisacrylamide (MBA), and gold metal. The effect of pDADMAc concentration to the actuator performance was investigated by using various amounts of pDADMAc. The chitosan-based film samples were characterized using FTIR, XRD, TGA, SEM, and DMA. The motion and force generation capabilities of the actuators were also investigated under electrical stimuli up to 17V. The suitability of the prepared chitosan-based films to be used as actuator for soft robotic applications is verified experimentally.

Acknowledgments
This study was supported by TUBITAK-The Scientific and Technological Research Council of Turkey, Project Number: 111M643.

P-85

APPLICATION OF LIGHT ACTIVATED LYSINE GRAFTED DEXTRAN NANOPARTICLES FOR TARGETED si_RNA DELIVERY IN NEUROSCIENCE

D. Zeini[a,b], J. Glover[a], B. Nyström[b]

[a]*Department of Phisiology, University of Oslo, Oslo, 0372, Norway*

[b]*Department of Chemistry, University of Oslo, Oslo, 0315, Norway*

(darya.zeini@medisin.uio.no)

Striking advances have been made in recent years in the areas of developmental neuroscience and the potential for stem cell-based treatment of neurological diseases. This is in large part based on the increasing power of high throughput gene sequencing technology to provide comprehensive gene expression and epigenetic profiles of selected cell populations. Using si-RNA molecules is a promising approach for knocking down or augmenting the expression of specific genes in selected endogenous neurons or in stem cell derived neurons *in vivo*. Temporal control and neuron target selectivity are the 2 main challenges in providing suitable siRNA delivery systems. As a non-viral Nano-delivery system we produced lysine grafted fluorescent dextran nanoparticles with the degree of substation of 0.54 to 1.26 of lysine per each Dextran chain. These free amines on the backbone of Dextran render a positively charged delivery vehicle which promotes complex formation and compression with the polyanionic siRNA. Moreover, the positive charge facilitates cell uptake by associating with the negatively charged cellular membrane. The next step is caging si-RNA with a photo- labile group, which will be conjugated on Dextran nanoparticles simultaneously. These photosensitive caged si-RNAs can retrogradely transport to neuronal cell body and be activated by delivering of light pulses via fiberoptic probes. This process does not involve the use of viruses or any permanent gene modification and if it is successful, it will provide a way to manipulate gene expression in specific neuron populations in human patients.

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P-86

NOVEL pH-SENSITIVE NANOCONTAINERS BASED ON EUDRAGIT/BRIJ98 MIXTURE FOR ORAL DRUG DELIVERY

A. Riabtseva, L. Kaberov, J. Kučka, M. Hrubý, S. K. Filippov

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(a.riabtseva@gmail.com, www.imc.cas.cz)

Oral drug delivery is the most popular method for inputting biological active substances into the body. The main obstacles for effective oral delivery of many drugs are their low stability at acidic pH in stomach, poor permeability across intestinal mucosa and proteolytic degradation which limit activity and duration of therapeutic effect.

The aim of this work was the development of novel effective pH-sensitive nanocontainers for oral drug delivery based on anionic polymer Eudragit L100-55 (poly(methacylic acid-co-ethyl acrylate) 1:1) and non-ionic surfactant Brij98. The features of interaction between Eudragit L100-55 and Brij98 at different pHs and their optimal ratio for nanoparticles formation were studied using isothermal titration calorimetry (ITC). Influence of the polymer-to-surfactant ratio on the size and structure of particles were studied at different pH values using dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) methods. It was shown that at the certain polymer-to-surfactant ratios stable nanoparticles at acidic pH are formed.

Trypsin was successfully encapsulated into Eudragit/Brij98 nanoparticles as a model drug. Loading efficiency was determined by labeling of trypsin with radioactive iodine ^{125}I.

Activity of loaded trypsin was evaluated after the treatment with digestive enzyme pepsin. Results showed that trypsin encapsulated into novel pH-sensitive nanocontainers preserve more than 90% of its activity after treatment with pepsin compared with non-encapsulated trypsin.

P-87

BIODEGRADABLE AND BIOCOMPATIBLE POLYMER NANOPARTICLES WITH FUNGAL BIOFILM INHIBITION AND MESENCHYMAL STEM CELL GROWTH CAPABILITIES

R. K. Donato[a], E. Jäger[b], A. Jäger[b], A. Höcherl[b], V. Z. Bergamo[c], A. M. Fuentefria[c], M. G. Raucci[d], L. Ambrosio[d], P. Štěpánek[b]

[a]Graphene and Nano-Material Research Center, MackGraphe, Mackenzie Presbiterian University, Rua da Consolação 896, São Paulo, Brazil.
[b]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
[c]Laboratory of Applied Mycology, Faculty of Pharmacy, UFRGS, Av. Ipiranga 2752, Porto Alegre, RS, Brazil
[d]Institute of Polymers, Composites and Biomaterials, National Research Council of Italy, Mostrad'Oltremare Pad.20, Viale Kennedy 54, Naples, Italy
(ricardo.donato@mackenzie.br, www.mackgraphe.mackenzie.br)

The [poly(alkene succinates)] based polyester nanoparticles (NPs) present innovative features as simple and cheap preparation, easy scaling-up, good mechanical and thermal resistance properties. They also present intrinsic *Candida* spp. biofilm inhibiting properties, reducing substantially the device-associated infections incidence.[1] Moreover, the NPs are highly biocompatible and promote human mesenchymal stem cell (hMSC) attachment and proliferation. Their self-assembly characteristics, which are highly dependent on the alkyl chain length, allow not only manipulating the NPs' morphology, but also inducing morphological changes in hMSC when in their presence. This makes the NPs promising candidates for materials in specialized medical devices and in the tissue engineering field.

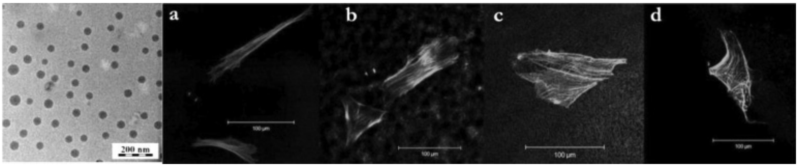

Figure 1. TEM image of biopolymer NPs (left) and confocal images of hMSC that developed in the presence of NPs with crescent alkyl chains (a-c) and reference PCL NPs (d).

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P-88

BIOCOMPATIBLE HAVOH/SILICA/IONIC LIQUID HYBRID'S INTERFACE BONDING

K. Z. Donato[a,b], R. K. Donato[a,#], M. Lavorgna[b], L. Ambrosio[b],
H. S. Schrekker[a], R. S. Mauler[a]

[a]*Institute of Chemistry, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, Brazil.*
[b]*Institute of Polymers, Composites and Biomaterials (IPCB) Portici, Italy.*
[#]*Current address: MackGraphe (Graphene and Nano-Material Research Center) Mackenzie Presbyterian University, São Paulo, Brazil.*
(zawada.kat@gmail.com)

Ionic Liquids (IL) are known polymer additives, either as plasticizers, lubricants, reinforcing and/or interfacial agents that improve, *e.g*., barrier, mechanical and thermal properties.[1] Due to their *self-assembly* properties, these IL act as dynamic-templates when applied at the initial steps of the sol-gel process, allowing controlling the silica particles' morphology, compactness and structure.[2]

Herein, IL were used as additives for biocompatible nanocomposites formation, based on highly amorphous vinyl alcohol (HAVOH) and silica, via *in situ* sol–gel process. The different IL functionalization (alkyl-, ether- or carboxylic) allowed controlling the silica structures and tune their interphase interactions. This resulted in the production of hybrids with excellent silica dispersion, as well as improved thermo-mechanical and water barrier properties. The polar group-functionalized IL induced the formation of multiple hydrogen bonding, producing significant increase in the storage and tensile moduli, extensibility and glass transition temperature, as well as a decrease in water vapor permeability, thus suggesting these nanocomposites' application for smart packaging.

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P-89

CHITOSAN-BASED HYDROGEL WITH A HIGH WATER UPTAKE CAPACITY FOR BIOMEDICAL APPLICATIONS

D. Aycan, N. Alemdar*

Chemical Engineering Department, Marmara University, Kadikoy,
Istanbul 34722, Turkey
(didem.aycan@marmara.edu.tr)

Hydrogels with high water uptake capacity could be prepared by polymer crosslinking that are able to release active species, such as therapeutic, antibacterial drugs [1]. In recent years, several hydrogel systems have been developed based on both natural and synthetic polymers. Among the natural polymers, chitosan and its derivatives have been extensively prefered due to their stimuli responsive properties (pH and temperature sensitivity). They can be modified owing to amine and hydroxyl groups which are present in their structure to enhance its physical and chemical properties such as solubility, swelling properties [2].

In this study, pH-sensitive chitosan-based hydrogels having high swelling capacity were synthesized. For this, glycidyl methacrylate (GMA), which is the acrylic monomer, was grafted on the chitosan backbone and thus CTS-g-GMA was produced in the first step. CTS-g-GMA and poly (ethylene glycol) diacrylate (PEGDA) were photopolymerized under the UV light. Following that the effect of parameters such as photopolymerization time, photoinitiator concentration, CTS-g-GMA/PEGDA ratio and polymer solution concentration on the swelling performance of hydrogel was investigated. According to the obtained results, optimum conditions for high water uptake capacity were determined. Hydrogel produced based on the optimum conditions would be used for conrtrolled drug delivery applicaitons in our future works.

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P-90

CONCENTRATION-MODULATION OF SELF-ASSEMBLY OF MONODISPERSE CARBON DOTS: FORMATION OF HIGH-BRIGHTNESS NANOAGGREGATES WITH FULL-COLOR EMISSION

T.-H. Chen[a,b], W.-L. Tseng[b]
[a]*Department of Chemistry, National Sun Yat-sen University, Taiwan*
[b]*Department of Chemistry, National Taiwan University, Taipei, Taiwan*
(tseng@mail.nsysu.edu.tw)

This study describes a bottom-up assembly route for monodisperse carbon dots (CDs) into different size of the CD aggregates. The highly monodisperse CDs were prepared via solvent-thermal treatment of edible soybean oil, which generated glycerol-based polymer as a carbon source and fatty acid as a surface capping in the synthetic process. The as-synthesized CDs exhibited small particle size variation (2.7–0.2 nm) and narrow emission bands (full width at half maximum <20 nm). The violet-emitting CDs (V-CDs) can self-assemble into blue- green-, yellow-, and red-emitting CD aggregates by increasing their concentration. Compared to commercial available organic dyes and semiconductor quantum dots,[1] the CD aggregates provided 10-to-7000-fold improvement in brightness. Additionally, their emission wavelength was tunable across the entire visible spectrum by tuning excitation wavelength. Because of their high brightness, fluorescent imaging of single CD aggregate was simply achieved using filter-free dark-field fluorescent microscopy (DFM).[2] We also demonstrate the use of filter-free DFM to dynamically image cellular uptake of V-CDs in the MCF-7 cells and Huh-7 liver cancer cells. Without the conjugation of fluorophore to the CDs, the particle aggregation-induced red-shift emission enables the development of CD-based ratiometric sensor for Fe^{III} and pyrophosphate based on Fe^{III}-induced aggregation of V-CDs.

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P-91

"ACTIVE SURFACES": BIOMOLECULE - POLYMER MEMBRANES FOR EFFICIENT SENSING OF PHENOLS

V. Mikhalevich[a], C. Draghici[b], J. Kowal[a], G. Gunkel-Grabole[a],
W. Meier[a], C. G. Palivan[a]

[a]*Department of Chemistry, University of Basel, Klingelbergstrasse 80*
CH-4056 Basel, Switzerland

[b]*Department of Product Design, Mechatronics and Environment,*
Transilvania Univ. of Brasov, 29 Eroilor Blv, 500036 Brasov, Romania

The design of surfaces that present active compounds at the interface with their environment is on focus today in various domains, such as catalysis, medicine or environmental sciences. An elegant approach is to combine biomolecules (enzymes, proteins, mimics) with synthetic membranes in order to generate a stable and functional hybrid system.[1]

Here we present how two different enzymes are combined with asymmetric membranes and serve for development of "active surfaces" for sensitive detection of specific compounds. Solid supported membranes of PEG$_{45}$-*b*-PMCL$_x$-*b*-PDMAEMA$_y$ copolymers were prepared by LB-LS methods in different combinations of conditions. Laccase and Tyrosinase, as model enzymes for detection of phenol compounds were immobilized on soft surfaces resulting from polymer films deposition. Interestingly, the enzymes activity and stability varied depending on the film properties, which support further optimization of such active surfaces.

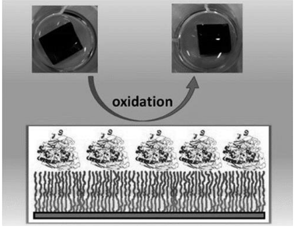

Figure 1: Oxidation of a phenolic compound by the active surface

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P-92

BIOPORES INSIDE SYNTHETIC MEMBRANES OF GIANT UNILAMELLAR VESICLES (GUVS)

M. Garni, M. Lomora, T. Einfalt, F. Itel, A. Dinu, W. Meier, C.G. Palivan

Chemistry Department, University of Basel, Klingelbergstrasse 80,
4056 Basel, Switzerland

Cells represent the fundamental structural and functional biologic unit with an autonomy provided by compartmentalization, which is based on the boundary lipid membrane with embedded membrane proteins serving for the molecular transport and communication between the inter and intra-cellular space. We introduced a biomimetic strategy to visualize transmembrane processes by insertion/reconstitution of biopores into synthetic membranes of cell sized giant unilamellar vesicles (GUVs) [1, 2, 3]. Here, we present how such biopores and membrane proteins inserted in thick synthetic membranes are functional, and allow diffusion of ions and molecules up to approximately 600 Da. Our sample pores are gramicidin [3] and ionomycin [4] as ion selective pores and the outer membrane protein F (OmpF). The latter allowed the diffusion of molecules up to 600 Da [5]. A key parameter in inserting biopores/membrane proteins in synthetic membranes is the flexibility and fluidity of the membrane, able to adapt in the region of the biomolecule [1, 2]. The insertion of biomolecules inside the membrane of GUVs serves for a rapid assessment of the biomolecule functionality via microscopy techniques. Our approach facilitates the control of specific catalytic reactions in confined spaces, selectively permeabilized to the substrates and products of the reaction: a deep insight of biological processes in real time can be obtained in this straightforward manner.

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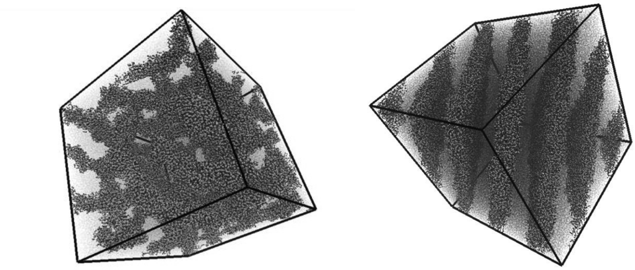
P-93

SELF-ASSEMBLY IN POLYELECTROLYTE MELTS: MESOSCALE SIMULATION

A. Gavrilov, A. Chertovich

Physics Department, Lomonosov Moscow State University, Leninskiye Gory 1-2, Moscow, Russia, 119991
(gavrilov@polly.phys.msu.ru)

The problem of microphase separation in polyelectrolyte copolymer blends has received massive attention during the last years due to the ability of such copolymers to form nonconventional structures. However, due to the overall complexity of the system there is no complete picture of the phase behavior even for the case of linear polyelectrolyte diblock-copolymers; moreover, the presence of two types of very distinct interactions (volume and electrostatic) makes it hard to develop a theory capturing all the relevant effects. We present a mesoscopic simulation of the phase behavior of linear polyelectrolyte copolymers. We use a well known dissipative dynamics method (DPD) which has been proven to be an excellent choice for simulation of melts of uncharged copolymers; the implementation of Coulombic interactions necessary to simulate polyelectrolytes is discussed. The phase behavior is studied for a number of chain compositions and interaction strengths; at low dielectric constants, the charge correlation effects cause the charged block with counterions to form a condensed phase, and the counterion entropy causes the system to adopt bicontinuous structures over a wide compositional window.



Examples of the structures obtained in a melt of polyelectrolyte copolymer with one charged block. Left: a bicontinuous structure; Right: a lamellar structure. Both of these phases are obtained at zero Florry-huggins interaction parameter χ.

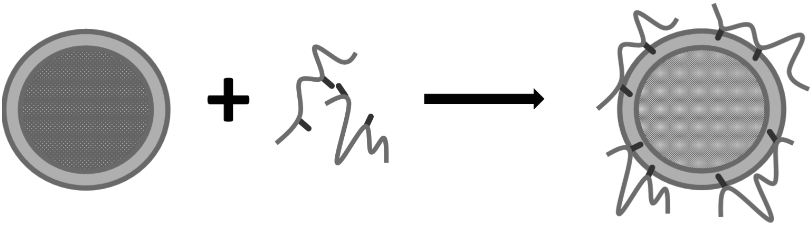
P-94

SELF-ASSEMBLY OF LIPOSOMES COATED WITH AMPHIPHILIC HPMA-BASED COPOLYMERS

O. V. Zaborova, S. K. Filippov, P. Chytil, T. Etrych

Institute of Macromolecular Chemistry, Czech Academy of Sciences,
Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(olya_z_88@mail.ru, www.imc.cas.cz)

Liposomes modified with polyethyleneglycol (PEG), so called “stealth”-liposomes, are used as the containers for drug delivery with prolonged longevity in the blood stream. The coating of liposomes by *N*-(2-hydroxypropyl)methacrylamide (HPMA) based copolymers is a promising alternative to the coating with PEG. Here, we report the physico-chemical study of self-assembly of HPMA-based amphiphilic copolymers bearing hydrophobic cholesterol moieties and liposomes. The main purpose of our research was a detailed investigation of formation of such hybrid complexes. The direct proof of interaction between liposomes and copolymers was obtained by isothermal titration calorimetry (ITC) measurements. Obtained ITC curves were analyzed to extract quantitative information about a number of copolymers needed to cover liposomal surface. For comparison, ITC experiments with titration of liposomes with PEG-cholesterol and Brij98 were conducted.



Violation of liposomal bilayer structure by embedded cholesterol moieties was witnessed by fluorescence experiments made with carboxyfluorescein (CF) loaded into liposomes with concentration above self-quenching. It was observed that the maximal release of CF from liposomes interior is strongly dependent on the copolymer/liposomes ratio in the system and did not exceed 20%. Such findings imply that liposomal membranes originally perforated by intrusion of cholesterol units were self-repaired due to intrinsic mobility of lipids.

P-95

SELF-ASSEMBLY OF CHLOROXINE INTO CRYSTALLINE NANOPARTICLES FOR WILSON'S DISEASE TREATMENT

T. Nejedlý, J. Trousil, M. Hrubý, Z. Walterová, M. Šlouf

Institute of Macromolecular Chemistry AS CR, v. v. i., Heyrovsky sq. 2,
Prague, 162 06, Czech Republic

Wilson's disease is a genetic disorder that leads to patologic accumulation of copper in organism and consequent toxic effects. Conventional therapy of Wilson's disease consists in suppression of absorption of copper by copper-chelating agents. Current therapies suffer from serious side effects. This contribution summarizes a study aimed on preparation and phisico-chemical characterization of sub-micronized chloroxine, that is an antibacterial drug, known under trade name such as Endiaron. Chloroxine works as copper-chelating bidentate ligand, thanks to the same structure 8-hydroxyquinoline motiv. In this study preparation of crystalline particles of chloroxine was optimised. The physico-chemical characterization of the chloroxine particles was carried out in terms of colloidal properties such as particle size, morphology, stability, particle size distribution, etc. and concurrently in terms of its abillity to copper chelatation.

P-96

DIELECTRIC PROPERTIES OF SILICA AEROGEL/POLYVINYLIDENE FLUORIDE (PVDF) COMPOSITES

D. Bozoğlu[a], *D. Değer*[a], *H. Deligöz*[b], *K. Ulutaş*[a]

[a]*Istanbul University, Science Faculty, Physics Department, General Physics Division Vezneciler -Istanbul 34459*

[b]*Istanbul University, Engineering Faculty, Chemical Engineering Department, Chemical Technologies Division Avcılar-Istanbul 34320*

Polyvinylidene Fluorıde (PVDF) is a widely used semi-crystalline polymer with good mechanical properties, resistance to chemicals, low dielectric constant and piezoelectric properties. Silica aerogel has low dielectric constant and hydrophobic structure In this study, the first surface modification at ambient pressure drying process performed with a superhydrophobic silica-based aerogels were synthesized. In different percentages of aerogel were homogeneously doped onto the PVDF and aerogels doped with different percentages polyurethane composite films were prepared. Using Alpha-A High Resolution Dielectric, Conductivity and Impedance Analyzer, dielectric constant and dielectric loss factor of samples were determined in the frequency range of 1Hz-1MHz and in the temperature range of 293K-473K with increment of 20K. The amplitude of AC voltage applied to samples was 1.0 V. Aerogel dopping effects on electrical properties of silica aerogel/PVDF composite films were also investigated to develop the end product which has lower dielectric constant for electrical insulating systems. In this context, the dielectric constant of the 1%, 2%, 3% and 4% aerogel doped PVDF was compared with neat PVDF at room temperature and found that dielectric constant was decreased silica aerogel doping.

P-97

PREPARATION AND ELECTRICAL BEHAVIOR OF OLEIC ACID COATED $CoFe_2O_4$ NANOPARTICLES DOPED INTO POLYESTER COMPOSITE FILMS

E. Özturk[a], T. Gürkaynak[b], H. Deligöz[b], M. Acikgoz[c], D. Deger[a]

[a]*Physics Department, Faculty of Science, Istanbul University, Istanbul 34134, Turkey*
[b]*Chemical Engineering Department, Engineering Faculty, Istanbul University, Istanbul 34320, Turkey*
[c]*Faculty of Engineering and Natural Sciences, Bahçeşehir University, Istanbul 34353, Turkey*

Ferrite compounds have been great interests due to their technological applications, such as magnetic and optical materials, semiconductors, pigments, catalysts or materials for biomedical applications. High molecular weight polymers (> 20000 Da) have been widely used as a soluble drug carries to improve drug targeting and therapeutic efficacy. In this study, pure polymer film and oleic acid coated cobalt ferrite doped into polymer composite film were prepared by solution casting method. Structural, morphological and dielectric properties of all polymer composite films were characterized. Firstly the oleic acid coated $CoFe_2O_4$ nanoparticles were synthesized by polyol method. The synthesized coated nanoparticles distributed into polymer matrix in 1% (wt/wt) proportions. For this purpose, polyester was used. For comparison pure polyester film was prepared.

The structures of the nanoparticles were characterized by X–Ray Diffraction (XRD), Fourier Transform Infrared with Attenuated Total Reflectance Unit (FTIR –ATR). Morphological properties of oleic acid coated nanoparticles were determined by scanning electron microscopy (SEM). The XRD pattern of the nanoparticles is consistent with standard $CoFe_2O_4$ (JCPDS no 22-1086) powder diffraction data without evidence of impurities. Fourier transform infrared measurements were carried out on the pure oleic acid and the $CoFe_2O_4$ coated with oleic acid nanoparticles to understand the absorption mechanism of oleic acid on the surface $CoFe_2O_4$ nanoparticles. We also analyzed the dielectric properties of the oleic acid coated nanoparticles in powder form and composite polymer films. Dielectric measurements were carried out in frequency range of 10^{-2} Hz -10MHz and in temperature range in 293K-373K. The dielectric constant (ε_1) of the all composite films and coated nanoparticles were determined by measured capacitance and dielectric loss factor. The measurements show that the dielectric constant of all samples decreases with frequency, whereas it increases with temperature.

P-98

PLASMA DISCHARGE POWER DEPENDENT ALTERNATIVE CONDUCTIVITY OF PLASMA POLYMERIZED POLYETHYLENE OXIDE (pPEO) THIN FILMS

S. Yakut, D. Değer, K. Ulutaş

Istanbul University, Science Faculty, Physics Department, General Physics Division Vezneciler -Istanbul 34459

Poly(ethylene oxide) (PEO) is a member of the large polymer family which draws attention with its non-fouling properties, the resistance against the adhesion of protein and cell onto surface of a material. The chemical composition of PEO can structure water in aqueous environment by causing non-covalent interaction with water. Thus possible bindings with proteins and cells are screened by PEO/water structure. Also the spiral shape of PEO enables repulsive interaction of macromolecules of PEO with proteins like a spring. However the macromolecules of PEO releases as a result of good solubility in aqueous solutions. Thus over long time periods the non-fouling properties decreases. Increasing the covalent bonding in Poly(ethylene oxide) is one of the possible way to improve the stability of Poly(ethylene oxide). This type of structure can be obtained by plasma polymerization. Deposition of plasma polymerized PEO samples were progressed by Plasma Assisted Physical Vapor Deposition (PAPVD) at low pressure. Samples were deposited between Aluminum (Al) electrodes in sandwich form as parallel plate capacitors. Plasma polymerization technique is a popular production way in the electronics and optics manufacturing industries. Alternative conductivity of capacitor samples were analyzed depending on frequency and temperature by Alpha-N broad frequency impedance analyzer. Applied voltage was 1 volt (rms). The frequency range was determined between 0.1 Hz–10^7 Hz and temperature range was between 193 K–253 K. Investigation showed that at low frequencies it is possible to observe accumulation of charges between electrode-sample interface. At mid frequency saturation region the mechanism corresponds to DC conductivity similar with the DC conductivity. At the high frequency dispersion region there is a mechanism which increases with increasing frequency and increasing temperature. The starting frequency for this region shifts through high frequencies at high temperatures. Obtained s values show a behaviour against temperature corresponding with Overlapped Large Polaron Tunneling (OLPT).

P-99

ANTITUBERCULOTIC RIFAMPICIN DRUG DELIVERY SYSTEM BASED ON POLYESTER NANOPARTICLES

J. Trousil[a], J. Matějková[b], S. K. Filippov[a], Z. Syrová[c], T. Mazel[c],
S. Svidenská[c], L. Kováčik[c], D. Cmarko[c], M. Hrubý[a], R. Lund[d],
B. Nyström[d], I. Raška[c], P. Štěpánek[a]

[a]*Institute of Macromolecular Chemistry AS CR, v. v. i., Heyrovsky sq. 2, Prague, 162 06, Czech Republic*
[b]*Department of Medical Microbiology, 2nd Faculty of Medicine, Charles University in Prague and Motol University Hospital, V Uvalu 84, Prague, 150 06, Czech Republic*
[c]*Institute of Cellular Biology and Pathology, Charles University in Prague, 1st Faculty of Medicine, Albertov 4, Prague, 128 01, Czech Republic*
[d]*Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway*

It is reported that about one-third of the world´s population has latent tuberculosis, a disease caused by causative agent *Mycobacterium tuberculosis*. The treatment of tuberculosis is difficult because of mycolic acids, one of the components present in the cell wall which are very hydrophobic and make the bacterial cell wall highly inpermeable. Problems in therapy of tuberculosis is concurrently given by the fact that *M. tuberculosis* cells are phagocytized by alveolar macrophages in which this intracellular pathogen persists and by multiresistance of the *M. tuberculosis* strains.

A relatively new and innovative approach for tuberculosis treatment are nanoparticle formulations of antituberculotics that would be targeted to the affected tissue in the lungs or even into the infected macrophages.

This contribution summarizes main results of a study aimed at development of a therapeutic system based on antituberculotic agent rifampicin encapsulated in biocompatible and biodegradable polymeric nanoparticles. The nanocarrier was prepared and characterised by light scattering methods and concurrently it was used for finding a suitable way for *in vitro* study of interaction of the nanoparticles with chosen cell lines that would be based on fluorescence resonance energy transfer approach (FRET).

NOTES

List of participants

Austria
Laffleur Flavia, University of Innsbruck, Innrain 80-82, 6020 Innsbruck

Brazil
da Silveira Nádya Pesce, Universidade Federal do Rio Grande do Sul, Ave. Bento Gonçalves, 9500, 91501-970 Porto Alegre

Donato Katarzyna Zawada, UFRGS, Av. Bento Gonçalves 9500, 91540-000 Porto Alegre

Donato Ricardo Keitel, MackGraphe (Graphene and Nano-Material Research Center), Mackenzie Presbyterian, Rua da Consolação 896, 01302-907 São Paulo

Silva Rafael, Avenida Joao Paulino Vieira 85, Apt 1201, 87020015 Maringa

Bulgaria
Marudova Maria Georgieva, Plovdiv University "Paisii Hilendarski", 24 Tzas Assen str., BG4000 Plovdiv

Canada
Fiurasek Petr, McGill University, Montreal

Zhao Yue, Department of Chemistry, University of Sherbrooke, Blvd. Universite, J1K 2R1 Sherbrooke

Croatia
Kratofil Krehula Ljerka, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb

Czech Republic
Delisavva Foteini, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague

Filippov Sergey, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Gospodinova Natalia, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Holubová Monika, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6

Hrubý Martin, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Jäger Alessandro , Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Jäger Eliézer, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Jůza Josef, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Konefał Rafał Łukasz, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Košovan Peter, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague

Kratochvíl Pavel, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Lang Jan, Charles University in Prague, Faculty of Mathematics and Physics, Dept. of Low Temperature Physics, V Holešovičkách 2, 180 00 Prague 8

Lemiech Sabina Jolanta, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Loukotová Lenka, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Nejedlý Tomáš, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Netopilík Miloš, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Nová Lucie, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague

Pánek Jiří, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Procházka Karel, Charles University in Prague, Department of Physical and Macromolecular Chemistr, Albertov 6, 128 43 Prague 2

Rabyk Mariia, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Riabtseva Anna, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Rutteová Michaela, Lach-ner, s.r.o., Tovární 157, 27711 Neratovice

Sedláček Ondřej, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Spěváček Jiří, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Stoy Vladimír A., MEDICEM Institute, Karlovarská třída 20, 273 01 Kamenné Žehrovice

Suchá Lucie, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague

Šindelka Karel, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague

Štěpánek Petr, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Tomšík Elena, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Trousil Jiří, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Vetrík Miroslav, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Wang Xiu, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague

Zaborova Olga, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Zhigunov Alexander, Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6

Denmark

Lee Seunghwan, Technical University of Denmark, Produktionstorvet, DK-2800 Kgs. Lyngby

France

Belbekhouche Sabrina, East Paris Institute of Chemistry and Materials Science, 2-8, rue Henri Dunant, 94320 Paris

Bernard Julien, IMP@INSA, 17 ave Jean Capelle, 69621 Villeurbanne

Borisov Oleg, IPREM/CNRS, 2 av. P.Angot, 64053 Pau

Deniau Elise, IPREM-UPPA, 5, avenue Pierre Angot, 64000 Pau

Gérard Jean-François, Directeur de la Recherche INSA Lyon, 37 avenue Jean Capelle, Bâtiment Direction, 69621 Villeurbanne cedex

Ghobril Cynthia, Loreal, 1 Avenue Eugene Schueller, Aulnay Sous Bois

Lacroix-Desmazes Patrick, Institut Charles Gerhardt - UMR5253 CNRS/UM/ENSCM, ENSCM, ICG-IAM, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5

Le Meins Jean-François, CNRS / University of Bordeaux, Laboratoire de chimie des polymères organiques, 16 avenue Pey-Berland, 33607 Pessac

Lecommandoux Sebastien, Université de Bordeaux, LCPO, ENSCBP, 16 Avenue Pey Berland, 33607 Pessac

Liao Yingjie, CERMAV-CNRS, 601 rue de la chimie, St Martin d'Hères, 38041 Grenoble

Lutz Jean-François, Institut Charles Sadron, 23 rue du Loess, 67034 Strasbourg

Nardin Corinne Cécile, Université de Pau et des Pays de l'Adour (UPPA)/Institut des Sciences Analytique, Hélioparc 2, av. Pdt Angot, 64053 Pau cedex 09

Schatz Christophe, Laboratoire de chimie des polymères organiques, CNRS - Université de Bordeaux, 16 Avenue Pey Berland, Pessac

Germany

Appelhans Dietmar, Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, Dresden

Ballauff Matthias, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin

Ehrmann Svenja, Freie Universität Berlin, Institute for Chemistry and Biochemistry, Takustr. 3, 14195 Berlin

Gumz Hannes, IPF Dresden, Hohe Straße 6, 01069 Dresden

Müller Axel H. E., Johannes Gutenberg University Mainz, Institute of Organic Chemistry, Duesbergweg 10-14, 55099 Mainz

Müller Marcus, Institute for Theoretical Physics, Georg-August University Göttingen, Friedrich-Hund-Platz 1, 37077 Goettingen

Papadakis Christine M., Technical University of Munich, Physics Department, James-Franck-Str. 1, 85748 Garching

Richtering Walter, RWTH Aachen University, Landoltweg 2, 52056 Aachen

Rossner Christian, Georg-August-Universität Göttingen, Institut für Physikalische Chemie, Tammannstraße 6, 37077 Göttingen

Schlegel Ralf, Fraunhofer-Institut für Mikrostruktur von Werkstoffen und Systemen IMWS, Walter-Hülse-Straße 1, 06120 Halle

Schmidt Sonja, Georg-August-Universitaet Goettingen, Insitute of Physical Chemistry, Karl-Grüneklee-Str. 8, 37077 Goettingen

Schoettner Sebastian, Technische Universität Darmstadt, Alarich-Weiss-Strasse 4, 64287 Darmstadt

Tian Jia, Institute of Physical Chemistry, Georg-August-University Göttingen, Tammannstrasse 6, 37077 Göttingen

Walther Andreas, DWI - Leibniz-Institute for Interactive Materials, Forckenbeckstr. 50, 52056 Aachen

Greece

Anastasiadis Spiros H., Foundation for Research & Technology - Hellas, Inst. of Electronic Structure & Laser, 100, N. Plastira Str., 71110 Heraklion Crete

Pispas Stergios, National Hellenic Research Foundation, Theoretical & Physical Chemistry Institute, 48 Vass. Constantinou Av., 116 35 Athens

India

Gupta Supriya, Indian Institute of Technology Delhi, Hauz Khas, 110016 New Delhi

Israel

Amir Roey Jacob, Department of Organic Chemistry, School of Chemistry, Tel Aviv University, 6997801 Tel Aviv

Italy

Bartolini Arianna, Department of Chemistry "Ugo Schiff" and CSGI, via della Lastruccia 3, 50019 Sesto Fiorentino

Japan

Labuta Jan, International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), 1-2-1 Sengen, 305-0047 Tsukuba

Netherlands

Tiwari Nitinkumar, Technische Universiteit Eindhoven, TNO 3.015, P.O. Box 513, 5600MB Eindhoven

Tuinier Remco, Eindhoven University of Technology, Groene Loper 5, 5600 MB Eindhoven

Voets Ilja, Eindhoven University of Technology, PO Box 513, 5600MB Eindhoven

Norway

Nyström Bo Örjan Gunnar, University of Oslo, Department of Chemistry, P.O. Box 1033, Blindern, N-0315 Oslo

Zeini Darya, University of Oslo, Sem Sælands vei 26, 0371 Oslo

People's Republic of China

Ai Ping, College of Chemistry and Chemical engineering, Yunnan Normal University, No.1 Yuhua Area,Chenggong District, 650500 Kunming City

Bi Yunmei, College of Chemistry and Chemical Engineering, Yunnan Normal University, No.1 Yuhua Area Chenggong New District, Box 2004, 650500 Kunming

Peng Xinyu, National Engineering Research Center for Biomaterials, Sichuan University, 29 Wangjiang Road, 610064 Chengdu

Sun Wei, Ningbo University, 818 Fenghua Road, 315211 Ningbo

Xu Long, National Engineering Research Center for Biomaterials, Sichuan University, 29 Wangjiang Road, 610064 Chengdu

Yan Jianqin, National Engineering Research Center for Biomaterials, Sichuan University, 29 Wangjiang Road, 610064 Chengdu

Zhang Yixin, National Engineering Research Center for Biomaterials, Sichuan University, 29 Wangjiang Road, 610064 Chengdu

Zhao Yan, College of Chemistry and Chemical Engineering, Yunnan Normal University, No1 Yuhua Area Chenggong New District, Box 2004, 650500 Kunming

Poland

Sikorski Andrzej, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw

Republic of Korea

Hong Sang Eun, Hannam University, 305-811, KS015 Yuseong-gu

Choi Jihoon, Chungnam National University, 99 Daehak-ro, 34134 Daejeon

Choi Seong-Ho, hannamUniversity, 305-811, KS015 Yuseong-go

Jang Kyung Ju, Hannam University, 305-811, KS015 Yuseong-gu

Kim Jinhwan, Sungkyunkwan University, Dept. of Polymer Sci. & Eng., Seobu-ro 2066, Jangan-gu, 16419 Suwon

Kim Tae-Hwan, KAERI, 1045 Daedeok-daero, Yuseog-gu, 34057 Daejeon

Kim Young-Wun, Korea Research Institute of Chemical Technology, Center for Biobased Chemistry, 141 Gajeong-ro, Yuseong-gu, 34114 Daejeon

Lee Sang Cheon, Kyung Hee University, 26 Kyungheedae-ro, Dongdaemun-Gu, 02447 Seoul

Lim Jong Choo, Dongguk University, Dept. of Chemical and Biochemical Engineering, 3-26 Phil-Dong, Choong-Ku, 100-715 Seoul

Ye JunHee, Hannam University, 305-811, KS015 Yuseong-go

Yoon Kuk Ro, Hannam University, 305-811, KS015 Yuseong-gu

Romania

Angelescu Daniel G., Institute of Physical Chemistry Ilie Murgulescu Romanian Academy, Splaiul Independentei 202, 060021 Bucharest

Cîrtoaje Cristina, Politehnica University of Bucharest, Splaiul Independentei No. 313, RO-060042 Bucharest

Russian Federation

Gavrilov Alexey A., Lomonosov Moscow State University, Leninskiye Gory, 1-2, Moscow

Govorun Elena Nickolaevna, Lomonosov Moscow State University, Faculty of Physics, Leninskie Gory 1-2, 119991 Moscow

Gubarev Alexander S., St. Petersburg State University, Universitetskaya nab. 7/9, 199034 St. Petersburg

Karpushkin Evgeny, Moscow State University, Leninskie Gory 1-3, 119991 Moscow

Khusnuriyalova Aliya, Kazan Federal University, Kremlyovskaya str., 18, 420008 Kazan

Markina Anastasia Alekseevna, Lomonosov Moscow State University, 119991 Leninskye Gory, 119991 Moscow

Obraztsova Nadezhda A., The Institute of Problems of Chemical Physics of the RAS, Academician Semenov avenue 1, 142432 Chernogolovka

Romanyuk Andrey Vladimirovich, M. V. Lomonosov Moscow State University, Polymer Department, Leniskiye Gory, 1, bld. 3, 119991 Moscow

Sybachin Andrey, M.V. Lomonosov`s Moscow State University, Leninskie Gory, 1-3, 119991 Moscow

Vasilevskaya Valentina, Nesmeyanov Institute of Organoelement Compounds RAS, ul. Vavilova 28, 119991 Moscow

Yaroslavov Alexander A., M.V. Lomonosov Moscow State University, Leninskie Gory, 1-3, 119991 Moscow

Sweden

Täuber Daniela, Lund University, Chemical Physics, PO-Box 124, 22100 Lund

Switzerland

Bösch Caroline D., Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern

Einfalt Tomaz, Department of Chemistry, University of Basel, Klingenbergerstrasse 80, Switzerland Basel

Gaitzsch Jens, University of Basel, Klingelbergstrasse 80, 4056 Basel

Garni Martina, University of Basel, Klingelbergstrasse 80, 4056 Basel

Chang Jui-Chia, École Polytechnique Fédérale de Lausanne, EPFL-STI-IMX-SMAL, 1015 Lausanne

Konishcheva Evgeniia, University of Basel, Klingelbergstrasse 80, Basel

Kownacki Mariusz, Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern

Lörcher Samuel, Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel

Mikhalevich Viktoria, University of Basel, Klingelbergstrasse 80, 4056 Basel

Palivan Cornelia G., University of Basel, Chemistry Department, Klingelbergstrasse 80, 4057 Basel

Taiwan

Chen Tzu-Heng, National Taiwan University, Chemistry department, No. 1, Sec. 4, Roosevelt Rd., 10617 Taipei

Chuang Wei-Tsung, National Synchrotron Radiation Research Center, 101 Hsin-Ann Rd., Hsin Chu

Tseng Wei-Lung, National Sun Yat-sen University, 80404 Kahosiung

Turkey

Alpaslan Duygu, Yuzuncu Yil University, Zeve Kampus, Van

Altınkaya Emine, Çanakkale Onsekiz Mart University Bioengineering department, Çanakkale

Aycan Didem, Marmara University, Istanbul

Demirel Adem Levend, Koç University, Rumelifeneri Yolu, 34450 Istanbul

Ersen Dudu Tuba, Yuzuncu Yil University, Zeve Kampus, Van

Gokce Gurcan, Yuzuncu Yil University, 65080 Van

İçli Özkut Merve, Yuzuncu Yil University, Tusba, 65080 Van

Ulutas Deniz Değer, Istanbul University, 34459, Istanbul

Ulutas Kemal, Istanbul University, 34459, Istanbul

United Kingdom

Boytsova Olga, Aston University, Aston Triangle, B4 7ET Birmingham

Gomez Magenti Jorge, University of Cambridge, Lensfield Road, CB2 1EW Cambridge

United States of America

Dormidontova Elena, University of Connecticut, Polymer Program, Institute of Materials Science and Physics Department, 97 North Eagleville Road, 06269 Storrs

Follmann Heveline Dal Magro, Aurora Street, 974 B, 08904 Highland Park

Kabanov Alexander V., University of North Carolina at Chapel Hill, 125 Mason Farm Road, Marsico Hall, Office 2201, CB#7362, 27599 Chapel Hill

Lee Kyung Sang, National Institutes of Health, 9000 Rockville Pike, Building 37 Room 3118, 20892 Bethesda

Lodge Timothy P., University of Minnesota, 207 Pleasant St SE, 55455 Minneapolis

Author Index

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Institute of Macromolecular
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Heyrovského nám. 2
162 06 Prague 6
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