

# IL 1 - Mon

## BIORESPONSIVE POLYMER THERAPEUTICS FOR TREATMENT OF CANCER AND FOR TISSUE REPAIR

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Having successfully transferred several families of HPMA copolymer anticancer conjugates into clinical trial [1], most recently HPMA copolymer platinates, we have now designed several families of bioresponsive polymer-protein conjugates containing biodegradable polymers more suitable for chronic administration. These are designed to treat cancer, arthritis, age-related macular degeneration and to promote tissue repair. Use of biodegradable polymers has brought a new approach for protein masking with triggered unmasking of pharmacological activity (PUMPT) [2-4]. Two models have so far been described; dextrin, which is degraded by  $\alpha$ -amylase [2-4], and hyaluronic acid, degraded by hyaluronidase [5]. Trypsin, MSH, rhEGF, phospholipase A<sub>2</sub> and ribonuclease conjugates have been described. Whereas conjugate is used to mask bioactivity and protect against proteolytic degradation, addition of the activating enzyme leads to a time-dependant reinstatement of protein bioactivity resulting in pharmacological response *in vitro* and *in vivo*.

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## IL 2 - Mon

### ENGINEERING NANO AND MACRO-SIZED "SMART" BIOMEDICAL STRUCTURES

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The term “thermo-responsive” refers to the ability of a polymeric system to achieve significant chemical, mechanical or physical transformations due to small temperature differentials. This feature of water soluble polymers can be harnessed to engineering both nano-metric as well as macroscopic biomedical systems. The “reverse thermo-responsive” phenomenon, usually known as Reverse Thermal Gelation (RTG), constitutes one of the most promising strategies available to researchers in this area. The water solutions of these materials display low viscosity at ambient temperature and exhibit a sharp viscosity increase as temperature rises within a narrow interval, producing semi-solid gels at body temperature.

This presentation introduces totally thermo-responsive nano-structures, comprising only poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblocks. The uniqueness of these novel nano-sized constructs stems from their ability to display a remarkable and reversible change in size (hundreds of times by volume), within a very narrow temperature interval. These supramolecular architectures are produced by cross-linking intra-micellarly end-capped PEO-PPO-PEO dimethacrylates, while these amphiphilic triblocks are constrained to the specific spatial configuration dictated by their micellar organization.

This contribution describes also several of the strategies pursued in our laboratory, aiming at tailoring the chemical, physical and biological properties of novel reverse thermo-responsive polymers, expanding, therefore, their clinical applicability. Particularly promising are: (i) The generation of RTG-displaying high molecular weight polymers, and (ii) The use of functionalized building blocks that combine thermo-responsiveness and in situ crosslinkability. Of special significance is the development of RTG-based in situ generated scaffolds for tissue engineering, as an alternative to the currently used pre-formed constructs comprising biodegradable polymers.

## IL 3 - Mon

### SUPRA-MACROMOLECULAR NANODEVICES FOR SMART MOLECULAR THERAPY

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The success in gene and nucleic acid delivery indeed relies on the development of the safe and effective carriers. In this regard, polyion complex (PIC) micelles, which are formed between nucleic acid and PEG-polycation block copolymers have received much attention due to their small size (~100 nm) and excellent biocompatibility. Recently, siRNA incorporated PIC micelle was prepared from PEG-poly(lysine) block copolymer with SH groups in the side chain. This PIC micelle is expected to release loaded siRNA selectively in cytoplasm due to the cleavage of disulfide crosslinking responding to the reductive intracellular environment, leading to the effective silencing of target gene related to oncogenesis. In turn, the disulfide crosslinking is stable enough in blood compartment to achieve prolonged circulation because of oxidized atmosphere in the body. These PIC micelles loading plasmid DNA or siRNA are now moving into in vivo evaluation for future molecular therapy. As the system particularly useful toward in vivo application, we developed a novel PEG-polycation block copolymer carrying the ethylenediamine moiety at the side chain (PEG-PAsp(DET)). Due to the regulated location of primary and secondary amino groups in a side chain, this block copolymer possessed both the sufficient DNA complexation ability and membrane disrupting capability selectively at endosomal pH, allowing the efficient endosomal escape of the polyplexes into cytoplasm. These properties of PEG-PAsp(DET) enabled the transfection to various primary cells. Notably, the PEG-PAsp(DET) polyplex micelles incorporating pDNA encoded with osteogenic factors were found to successfully transfect recipient cells in mouse calvaria bone defects to induce bone regeneration, demonstrating their utility in the field of tissue regeneration.

## IL 4 - Mon

### DYNAMIC POLYMERS FOR THERAPEUTIC DNA AND RNA DELIVERY

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Viruses change their properties during the infection process, to make them most effective for the individual different cell entry steps. Inspired by natural processes such as viral cell entry, synthetic polymer-based nanoparticles can be chemically programmed for effective delivery of therapeutic nucleic acids such as pDNA or siRNA [1]. For this purpose polymeric carriers are equipped with chemical molecular sensors (such as pH-sensitive conformations or covalent bonds) able to respond to the relevant endogenous biological triggers (e.g. endosomal acidification) or, alternatively, physical stimuli (e.g. hyperthermia). For example, EGF containing polyplexes reversibly shielded with an endosomal pH-labile pyridylhydrazone-based PEG reagent mediate an enhanced tumor specific transgene expression after intravenous administration in a subcutaneous HUH7 tumor model in SCID mice as compared with stably shielded polyplexes [3]. Alternatively, acetal groups have been incorporated into gene carriers [4-5] to trigger disassembly in the endosomal compartment. The specific and effective cellular uptake by the EGF receptor was utilized for therapeutic delivery of double stranded RNA poly-IC [4]. Transferrin-coated siRNA polyplexes were applied for therapeutic delivery of RAN siRNA into tumors [6]. Dynamic polyplexes for improved siRNA delivery and intracellular release [7] will also be presented.

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# IL 5 - Mon

## TARGETED NANOMEDICINES AND EC-SPONSORING IN FP6

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Many candidate and established drugs have inferior properties with consequently unfavourable therapeutic implications. Nanoparticulate drug targeting systems (targeted nanomedicines) can be designed to improve the therapeutic behaviour of such drugs. Nanotechnology-inspired approaches to particle design and formulation, an improved understanding of (patho)physiological processes and biological barriers to drug targeting, as well as the lack of new chemical entities in the 'pipeline' of large pharmaceutical companies, indicate that there is a bright future for targeted nanomedicines as pharmaceuticals. A multidisciplinary research approach, employing the combined forces of many scientific disciplines, is a key factor for success. It is becoming increasingly recognised that a major limitation, impeding the entry of targeted delivery systems into the clinic, is that new concepts and innovative research ideas within academia are not being developed and exploited in collaboration with the pharmaceutical industry. Thus, an integrated 'bench-to-clinic' approach realised within a structural collaboration between industry and academia, is required to safeguard and promote the progression of targeted nanomedicines towards clinical application.

The development of effective, safe, and innovative drug targeting systems, is a complicated multi-step process. There is an increasing need to select and / or identify appropriate matrix materials, surface coatings, and targeting ligands with advanced properties. Therapeutic agents (small molecules, but also macromolecules like proteins and nucleic acids) to be loaded into nanocarriers vary widely in their physicochemical properties and it remains a challenge to balance the nanoscale dimensions of the particulate with the types and amounts of drugs that are clinically required. Proper structural and physicochemical characterisation is required to guarantee reproducible effects *in vivo*. Advances in particle engineering (e.g. surface modification with 'stealth' polymers, like poly(ethyleneglycol) (PEG) and targeting ligands) have already yielded nanoparticles which can reach major pathological sites *in vivo*, after intravenous and local routes of injection.

MEDITRANS represents a multidisciplinary Integrated Project sponsored by the EC (FP6) dealing with targeted nanomedicines. Platform technologies are being developed with broad applicability to disease treatment, as exemplified by the choice for chronic inflammatory disorders (rheumatoid arthritis, Crohn's disease, multiple sclerosis), and cancer as target pathologies. Nanomedicines (based on carrier materials like polymeric and lipidic nanoparticles, nanotubes, and fullerenes) will be endowed with superior targeting and (triggerable) drug release properties. In parallel, MRI imaging probes will be designed that report on the *in vivo* localization of the targeted nanomedicines, specific biomarkers, the drug release process and therapeutic outcome (imaging-guided drug delivery). The consortium consists of 30 partners from 9 EU member states (including 1 new member state) and 3 associated states, and includes 13 industrial companies, 11 universities and 6 research institutes. This lecture will discuss selected examples of targeted anti-inflammatory nanomedicines being investigated within the MEDITRANS project.

## IL 6 - Mon

### POLYMER BRUSHES AS RESPONSIVE MATERIALS FOR THE BIOLOGY-MATERIALS INTERFACE

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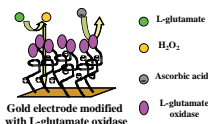
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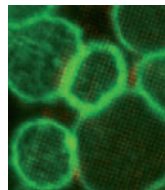
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The control of the physicochemical properties of surfaces in contact with biological systems represents a fundamental issue in many applications ranging from coatings to biotechnology and microelectronics. In particular, advances in nanobiotechnology depend on the ability to fashion materials with precise control of feature size and functionality. This presentation focuses on issues of specific and non-specific binding and strategies being developed to control both. Methods of characterizing these surfaces will also be described including synchrotron based NEXAFS and GISAXS.

Examples of specific binding that enable investigation of cell function will be presented. The broader issue of non-specific binding and how it relates to fouling release will also be discussed in terms of surface structure. Both polar and non-polar surfaces have been investigated and each type shows promise for release specific biological systems. In particular, polymer brushes grown from silicon surfaces have been shown to be especially effective<sup>i</sup> and their use for control of cell-surface interactions will be discussed.



**Fig. 2** Scheme for successful screening of charged ascorbic acid using polymer brushes in glutamate sensor



**Fig. 1** Mast cell in contact undergoing surface-induced degranulation

The self-assembly of block copolymer thin films enables the creation of brush-like polymer surfaces<sup>ii</sup>. The identification of a “universal” surface for release of all biological systems remains elusive. New coatings that make use of recent discoveries in improved fouling release based on dynamic surfaces will also be described<sup>iii</sup>. These materials may form the basis of environmentally friendly fouling release coatings for marine and biomedical applications.

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## IL 7 - Mon

### BIOINSPIRED SYNTHESIS OF COMPLEX FUNCTIONAL SYSTEMS

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Our laboratory is involved in the use of biological systems as models for the elaboration of new concepts at the interface between macromolecular, supramolecular and biological sciences by using self-assembling non-biological macromolecules as building blocks. These concepts are subsequently used in the design of nanostructures, and functional complex systems by following the biological principles “structure determines functions”. This lecture will first discuss the principles used in the design, synthesis of libraries of self-assembling building blocks via structural and retrostructural analysis. Subsequently the use of these building blocks for the elaboration of non-biological chiral complex systems (*Science* **1997**, 278, 449-452; *Nature* **1998**, 391, 161-164; *Nature* **2002**, 419, 384-387; *Science* **2003**, 299, 1208-1211; *Nature* **2004**, 428, 157-160; *Nature* **2004**, 430, 764-768; *PNAS* **2006**, 103, 2518-2523; *JACS* **2007**, 129, 11265-11278; *JACS* **2007**, 129, 11698-11699; *JACS* **2008**, 130, 7503-7508; *JACS* **2008**, 130, 13079-13094; *JACS* **2008**, 130, 14840-14852; *JACS* **2009**, 131, 1294-1304) that exhibit biological functions will be elaborated.

## IL 8 - Mon

### MAKING POLYMERS SWIM

A.J Ryan

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The potential dangers of Nanotechnology has been in the news a lot recently. The fear of the world being overrun with "grey goo" was even highlighted by our HRH Prince Charles. This fear has to be balanced against all the potential benefits we hear that nanotechnology will bring, in medicine and the environment, with nanomachines saving lives and cleaning up pollution. We will review the current state of the art, in consumer goods, medicine, and energy management, seeing where the first applications of Nanotechnology might be. We will ask the question "what will a nanobot look like?". Will it be the shrunken submarine envisaged by Hollywood and on the internet? I don't think so. But what will it be? We think something soft and wet, just like biology, and have built a series of biomimetic devices. Our progress in the development of molecular devices based on responsive polymer gels and motile particles will be discussed.

A scalable synthetic muscle has been constructed that transduces nanoscale molecular shape changes into macroscopic motion. The working materials, which deform affinely in response to a pH stimulus, are self-assembled block copolymers comprising nanoscopic hydrophobic domains in either a weak polyacid or a weak polybase matrix. Devices have been assembled where the muscle does work on a cantilever and the force generated has been measured. When coupled to a chemical oscillator this provides a free running chemical motor that generates a power by the serial addition of 10nm shape changes that scales over five orders of magnitude. It is the nanostructured nature of the the gel that gives rise to the affine deformation and results in a robust working material for the construction of scalable muscle devices. A "push-me pull-you" device has been constructed such that the simultaneous expansion and contraction of polyacid and polybase materials are coupled in response to an oscillating reaction.

The motion of an artificial microscale swimmer that uses a chemical reaction (decomposition of hydrogen peroxide) catalyzed on its own surface (a platinum patch on a polystyrene particle) to achieve autonomous propulsion is fully characterized experimentally. It is shown that at short times it has a substantial component of directed motion, with a velocity that depends on the concentration of fuel molecules. At longer times, the motion reverts to a random walk with a substantially enhanced diffusion coefficient.

These results suggest strategies for designing artificial chemotactic systems.



## IL 9 - Tue

### **ION-TRANSPORT IN POLYMERS: HOW TO IMPROVE THE PERFORMANCE OF BATTERIES AND FUEL-CELLS?**

G. Wegner

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Facile ion transport is key to the performance of Lithium-based storage batteries and polyelectrolyte-membrane fuel cells (PEMFCs). The mechanisms of ion-transport in polymer materials give an indication how better and more efficient materials can be designed. This has a considerable on technology development, wherever production and storage of electrical energy on-site and on-time is required. This is the case for the automobile industry as well as for the electronic industry in so far as mobile devices are concerned.

Recent synthetic and physico-chemical progress towards novel proton-conducting polymers as well as Lithium-ion conducting polymers will be presented in the light of the demands of the relevant industries.

# IL 10 - Tue

## **POLYMER BRUSHES IN CONFINED ENVIRONMENTS: NEW CHALLENGES AND OPPORTUNITIES FOR DESIGNING ADVANCED FUNCTIONAL MATERIALS**

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The rational design of robust platforms enabling the selective transport of ionic species has received considerable attention during the last decade. This interest stems from the wide variety of technological applications relying on “gated” transport processes, such as ultrafiltration or controlled delivery. The generation of interfaces discriminating the transport of cationic and anionic species, i.e.: permselectivity, is an intrinsic mechanism of nature, as can be seen in cornea or human skin which exploit fixed charges in the membrane to generate differential permeabilities. When dealing with synthetic materials, manipulating chemistry and topology down to the nanoscale is essential to achieve this goal and, as such, represents one of the ongoing challenges in materials science.

In this presentation we will discuss different routes to manipulate and control the transport of different chemical species by assembling “smart” or “intelligent” active structures, with agile response to minute environmental changes, into nanoconfined environments. Within this proposed framework we will describe the use of photoelectrochemically etched substrates,<sup>[1]</sup> solid-state nanopores<sup>[2]</sup> and mesoporous films<sup>[3]</sup> as scaffolds for creating robust and shape-persistent nanoscopic channels. We will show that the incorporation of adaptive and responsive soft materials into the robust nanoscopic channels provides new opportunities to molecularly design hybrid assemblies with controllable transport properties.

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## IL 11 - Tue

### MOLECULAR ENGINEERING OF CELLULAR ENVIRONMENTS: CELL ADHESION TO NANO-DIGITAL SURFACES

Joachim P. Spatz

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Engineering of cellular environments has become a valuable tool for guiding cellular activity such as differentiation, spreading, motility, proliferation or apoptosis which altogether regulates tissue development in a complex manner. The adhesion of cells to their environment is involved in nearly every cellular decision in vivo and in vitro. Its detailed understanding and defined control also opens new strategies for medical technologies with respect to, e.g., stem cell regulation, tissue scaffolds, cell selection due to their disease state, artificial blood vessels, or immunology.

Our approach to engineer cellular environments is based on self-organizing spatial positioning of single signaling molecules attached to inorganic or polymeric supports, which offers the highest spatial resolution with respect to the position of single signaling molecules. This approach allows tuning cellular material with respect to its most relevant properties, i.e., viscoelasticity, peptide composition, nanotopography and spatial nanopatterning of signaling molecules. Such materials are defined as “nano-digital materials” since they enable the counting of individual signaling molecules, separated by a biologically inert background. Within these materials, the regulation of cellular responses is based on a biologically inert background which does not trigger any cell activation, which is then patterned with specific signaling molecules such as peptide ligands in well defined nanoscopic geometries. This approach is very powerful, since it enables the testing of cellular responses to individual, specific signaling molecules and their spatial ordering. Detailed consideration is also given to the fact that protein clusters such as those found at focal adhesion sites represent, to a large extent, hierarchically-organized cooperativity among various proteins. Moreover, “nano-digital supports” such as those described herein are clearly capable of involvement in such dynamic cellular processes as protein ordering at the cell’s periphery which in turn leads to programming cell responses.

## IL 12 - Tue

### FUNCTIONAL MATERIALS FOR FUTURE DEVICES

G. Nelles

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An overview about the research activities at the Materials Science Laboratory (MSL) of Sony on functional materials for future applications will be given. MSL is one of the Sony Corporate R&D Laboratories under the umbrella of the Advanced Materials Laboratories (AML) located in Japan. Macromolecules are to be found in many of the Sony products such as displays, batteries, etc. Representative examples of the research on macromolecules will be given. In particular activities in the fields of display technologies and organic electronics will be presented.

In display technology MSL focuses on two subjects: LCD and paper like displays. Alignment of liquid-crystal (LC) materials is one of the most important issues in LCD fabrication. The polymers used as alignment materials in LCDs directly affect the contrast of the displays and play a crucial role in the response properties of LC materials. Clever design and tuning of these polymeric alignment materials can improve both the contrast and the response speeds of LC displays. On the other hand, dispersing the LCs in small droplets into a polymer matrix results in a so called polymer dispersed liquid crystal cell. By doping the PDLC with dichroic dyes, the films exhibit an absorbing off-state and a transparent on-state. Such films offer a promising technology in application areas such as e-paper.

Re-configurable electronic circuits are used to shorten the development time for new products and to decrease the production costs. However, re-configurable circuits used nowadays lack high integration densities. In the presentation, a new combination of transistors with resistive switching elements is described which allows building dense and fast re-configurable devices.

## IL 13 - Tue

### TOWARDS STABLE BLUE LIGHT-EMITTING MATERIALS

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Polymer light emitting materials have received remarkable attention because of their potential applications in large-area flat-panel displays. Three primary colors, i.e., blue, green, and red emitting materials, are essential for full-color displays. Green and red light emitting materials have been already achieved with high brightness and efficiency. However, blue light emitting polymers fully meets requirements for commercially feasible light emitting diodes are very scarce. A challenging goal in this area is to achieve blue light emitting materials with long-term stability, high efficiency, and free of blue-green emission. To achieve stable blue light emitting materials, we have designed and synthesized three-dimensional hyperbranched polyfluorenes, dendronized polyfluorenes, spirobifluorene-based polymers, and spiro-bridged ladder poly-*p*-phenylenes.<sup>1-6</sup>

For blue light-emitting hyperbranched polyfluorenes, they could form good quality amorphous films and exhibit very good luminescent stability. Using a device configuration of ITO/PEDOT/polymer/Ca, a luminance of more than 3000 cd/m<sup>2</sup> and an external quantum efficient yield of 2.46% were obtained. Compared with the linear polyfluorenes, significant improvement has been achieved.<sup>1,3</sup>

We have demonstrated that spirobifluorene structure could significantly suppress the formation of ketonic defect and endowed the polymer with good color stability. The unusual rigid three-dimensional structure makes spirobifluorene an ideal building block in construction of stable blue-light emitting and plastic laser materials. The spiro-concept can overcome the photo/thermal oxidation of 9-position of fluorene unit to the undesired ketonic defect. We report here the synthesis of ladder-type oligomers and polymers based on spirobifluorene units.<sup>4-6</sup>

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## IL 14 - Tue

### NANO-SCALE STRUCTURE OF POLYMER AMPHIPHILIC SYSTEMS: TAILORED NEW PHASES AND APPLICATIONS AS SMART MATERIALS

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The phase behaviour of diblock block copolymer systems and simple amphiphiles are by now rather well understood both theoretically and experimentally, including the nanoscale ordered phases: lamellar, body centred cubic structure of spherical micellar, hexagonal packed cylinders, and the more complex gyroid and modulated lamellar phases near the boundaries [1]. Using external fields it is possibly to control the morphology further [2]. Going beyond simple linear diblock copolymers gives potential for a large variety of new phases. Examples are star-shaped molecules consisting of more than 2 mutually immiscible polymer blocks. As a consequence of the star-shaped geometry, such polyphiles self-assemble along one-dimensional lines, and not along surfaces as in the case of linear block copolymers [3]. A wealth of possible novel nanostructures are predicted. We will review some recent results on both linear and star shaped polymer block copolymer systems, and discuss their stability versus mechanical treatment and chemical additives [4,5]. We will further discuss the potential use of block copolymers as templates for smart membrane materials [6].

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## IL 15 - Tue

### **HYBRID BLOCK GYLCOPOLYMER SELF-ASSEMBLIES**

R. Borsali

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This presentation will be focused on *Challenges at the Nanoscale Level in Oligosaccharides and Polysaccharides Systems*. The talk will emphasize on how to prepare nanoparticles and nanostructured films made from oligosaccharides or polysaccharides. During the past decades, a slight chemical modification, generally a link of few hydrophobic groups along the main polysaccharide backbone, induces a dramatic change on the structure and the dynamics of the modified polysaccharides : These are the so-called “Self-associative” systems at the origin of many industrial applications (food, cosmetic, oil recovery, medical,...). Today, the main challenge is to design new architectures molecule-based oligosaccharides or polysaccharides: “hybrid block copolymer”. Such systems exhibit a remarkable capacity to **self-assemble** into a great variety of macromolecular structures both in the solution (nanoparticles) and bulk state (thick and thin films), whose dimensions span from few to hundred nanometres. Their final nano-organization results from the interaction between the molecular species and architecture, the block composition and, in the case of solution, the affinity of the solvent for the different blocks. In the bulk, the regular long range ordered structures are commonly used to create thin films and build new **controlled nanometer-sized** materials, which found a number of key applications, spanning from pharmaceutical, biomedical engineering to microelectronics where the control at the nanoscale 2D and 3D level is of great importance. Some results on glyco-hybrid block copolymer systems will be presented.

## IL 16 - Tue

### **BLOCK COPOLYMER MICELLES WITH COMPLEXED METALLACARBORANES IN CORES**

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Polyhedral metallacarboranes (e.g., the Co-containing metallacarborane COSAN) exhibit high hydrophobicity, rigid geometry, partially delocalized negative charge, ion-pairing behavior and strong acidity of conjugated acids. Recently they have been recognized as potent inhibitors of HIV protease. For several years, we have been studying the association of metallacarboranes and their interaction with water-soluble polymers. In this presentation, we report on the formation of COSAN-containing multimolecular micelles of polyoxyethylene-*block*-poly(methacrylic acid), PEO-PMA as a result of the formation of an insoluble COSAN-PEO complex upon mixing aqueous COSAN (Na salt) and alkaline PEO-PMA solutions. The micelles contain cores formed by the COSAN-PEO complex and PMA shells. They are fairly large, but reasonably monodisperse (hydrodynamic radius,  $R_H$ , measured by dynamic light scattering ca.  $10^2$  nm).

The formation of the COSAN-PEO complex can be supported by quantum mechanics calculations which predict that H atoms attached to B bear a non-negligible negative charge and form dihydrogen bonds with positively charged hydrogen atoms (in OH, NH and O-CH<sub>2</sub>).



## IL 17 - Tue

### **POLYMER THERAPEUTIC ARCHITECTURE: A MAJOR FACTOR IN ACHIEVING HIGHLY EFFICIENT POLYMER MEDICINES**

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In the last three decades a number of water-soluble synthetic polymers have been studied as drug carrier systems suitable for delivery of various types of therapeutics. Conjugation of drugs with water-soluble polymers may reduce their toxicity, improve solubility, bioavailability and stability (enzymatic, thermal), eliminate undesirable body interactions, prolong blood circulation and improve specificity of the drug biodistribution. To reach a tumour tissue-specific or a tumour cell-specific drug accumulation a well-considered selection of the polymer carrier structure and targeting strategy is important. The antitumour efficiency of the polymeric prodrugs intended for treatment of solid tumours can be further improved by increasing molecular weight of the polymer carrier, evoking better tumour accumulation of the prodrug due to the enhanced permeability and retention (EPR) effect.

Here, we present various structures of drug delivery systems based on *N*-(2-hydroxypropyl)methacrylamide copolymers, namely with the aim to show the impact of the conjugate structure on its physico-chemical and biological properties. Different systems intended for solid tumor accumulation are displayed, starting from simple linear polymers to the more sophisticated biodegradable grafted and dendritic high-molecular-weight polymer conjugates. Also in antibody (Ab)-mediated active targeting of polymer-drug conjugates the conjugate architecture strongly influences specificity of the drug action and treatment effects of such targeted system. Diverse methods of Ab attachment to the polymer carrier and relation between method of Ab attachment and ability of the conjugate to bind to cancer cell receptors in vitro and exhibit in vivo anticancer activity are described. Last but not least effect of drug combination or type of drug attachment on the antitumor efficiency is showed.

**Acknowledgement:** The work was supported by the Grant Agency of Academy of Sciences of the Czech Republic (grant No. IAA400500806), by the Ministry of Education, Youth and Sports of the Czech Republic, through the program “Research Centers” (grant No. 1M0505).

## IL 18 - Tue

### HOW THE INSTITUTE OF MACROMOLECULAR CHEMISTRY INSPIRED AND INFLUENCED MY RESEARCH OVER THE PAST 40 YEARS

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My initial involvement with the Institute of Macromolecular Chemistry (IMC) in Prague began on paper in the late 1960s. We had all heard about the PHEMA soft contact lens of Prof. Otto Wichterle, and I was writing a research proposal to the US Atomic Energy Commission to support the preparation of biocompatible and bioactive biomaterials by  $^{60}\text{Co}$  radiation-grafting HEMA monomer to hydrophobic biomaterials such as silicone rubber or polyethylene (PE), in order to enhance the biocompatibility of those materials. The surface-grafted PHEMA also provided hydroxyl groups for the subsequent covalent attachment of biomolecules such as heparin and fibrinolytic enzymes as streptokinase.

About fifteen years later, in the early 1980s, I was looking for a phase-separating polymer that I could conjugate a capture antibody to, in order to develop a new, phase-separation immunoassay. In early work with PHEMA in the mid-1970s, my postdoc Buddy Ratner had noticed that PHEMA phase-separated as it polymerized. So I began development of my new immunoassay by conjugating HEMA monomer groups to an antibody, allowing the antibody to bind its target antigen, and then copolymerizing it with free HEMA to phase-separate the immune complex. This assay worked well, but the process became difficult to control due to the interference of traces of oxygen and impurities. Fortunately, around the same time Jim Guillet introduced me to PolyNIPAAm and its thermal phase-separating properties. That led me to the earlier seminal literature of Karel Dusek, who had predicted discontinuous phase transitions in polymers, and from there on to Toyo Tanaka's beautiful demonstration of discontinuous transitions with PNIPAAm. This was the beginning of my long love affair with the smart polymer, PNIPAAm.

Since the early 1990s I have been collaborating with Pat Stayton at UW on intracellular delivery of nucleic acid, peptide and protein drugs. We are using polyHPMA as a block in our block copolymer nanocarriers. This is another unique IMC polymer, invented by Jindra Kopecek and Karel Ulbrich and coworkers at IMC.

My presentation will cover our involvements with IMC polymers over the years, and our continuing work with them.

## IL 19 - Wed

### NEW SOLID-STATE NMR METHODOLOGY FOR PROBING STRUCTURE-DETERMINING HYDROGEN-BONDING INTERACTIONS

S. P. Brown

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Solid-state MAS NMR experiments utilising recently developed methodology such as homonuclear  $^1\text{H}$  decoupling and through-bond  $J$  correlation are yielding new insight into hydrogen bonding interactions that control the packing of organic molecules into three-dimensional structures.

Specifically, the  $^1\text{H}$  chemical shift is a sensitive indicator of hydrogen-bonding strength and aromatic pi-pi interactions, with high-resolution  $^1\text{H}$  double-quantum (DQ) experiments enabling the identification of proton-proton proximities [1]. Indeed, a combined experimental and computational approach reveals changes in the  $^1\text{H}$  chemical shift of  $> 2$  ppm due to weak hydrogen bonding, e.g.,  $\text{CH}\dots\text{O}$  [2,3].

Complementary information is yielded from  $\text{NH}\dots\text{N}$  and  $\text{NH}\dots\text{O}$  hydrogen-bond mediated  $2h\text{JNN}$  and  $2h\text{JNO}$  couplings [4,5]: hydrogen-bonding partners can be unambiguously identified in refocused INADEQUATE spectra, while hydrogen-bonding strength can be quantified by the measurement of the  $J$  couplings in spin-echo experiments. Specifically, different intermolecular hydrogen-bonding arrangements as well as their strength have been determined in synthetically modified guanosines, so as to identify different modes of self-assembly, namely quartet or ribbon formation [4,6].

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## IL 20 - Wed

### NANOSTRUCTURED POLYMER SYSTEMS AS SEEN BY SOLID-STATE NMR SPECTROSCOPY

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One of the current trends in macromolecular chemistry is the design of multiphase nano-heterogeneous materials with tunable properties. Besides a large synthetic effort, the achievement of this target must be supported by the deep characterization of resulting products. As a contribution to this trend an application of recently developed solid-state NMR techniques based on measurements of dipolar couplings will be presented.

Recent methodological advances improved sensitivity and resolution in  $^1\text{H}$  frequency dimension in such a way that the obtained highly-resolved  $^1\text{H}$ -X correlation spectra provide sufficient number of dipolar contacts. The extracted distance restrains then can be used to reconstruct basic structural motifs. Several examples of utilizations of these heteronuclear correlation experiments will be demonstrated. Dipolar couplings give not only interatomic distances. From the averaging of dipolar couplings motional amplitudes of molecular segments can be derived. Recently we have developed pulse sequences designed for the “domain-selective” measurements of heteronuclear dipolar interactions in mobile amorphous and/or rigid crystalline phases [1]. In this way the amplitudes of segmental motions in heterogeneous polymer nanocomposites below as well as above glass-transition temperature have been successfully described [2,3]. It will be also demonstrated that the applied dipolar recoupling experiments yield valuable data that can be related to the mechanical and thermomechanical properties of polymer nanocomposites. Finally, the concept of NMR crystallography will be discussed.

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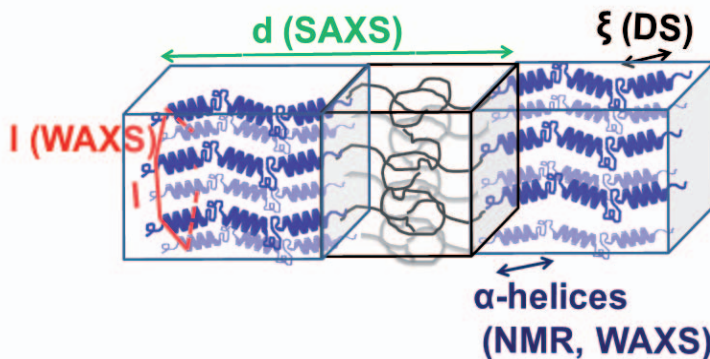
## IL 21 - Wed

### SELF-ASSEMBLY AND DYNAMICS OF SYNTHETIC POLYMERS AND POLYPEPTIDES FROM NMR SPECTROSCOPY

H.W. Spiess

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This talk highlights the results of recent efforts on understanding the hierarchical self-assembly and dynamics of polypeptides with the aid of different NMR techniques, X-ray scattering and dielectric spectroscopy.<sup>1</sup> The concerted application of these techniques shed light on the origin of the glass transition, the persistence of the  $\alpha$ -helical peptide secondary motif and the effects of topology and packing on the type and persistence of secondary structures. With respect to the freezing of the dynamics at the liquid-to-glass temperature it was found that the origin of this effect is a network of broken hydrogen bonds. The presence of defected hydrogen bonded regions reduces the persistence length of  $\alpha$ -helices. Block copolypeptides provide means of manipulating both the type and persistence of peptide secondary structures.



**Figure 1.** Assembly of a lamellar hybrid polypeptide-coil diblock copolymer depicting the main techniques employed in this study, small-angle and wide angle X-ray scattering (SAXS, WAXS),  $^{13}\text{C}$  NMR and dielectric spectroscopy (DS).

Review

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## IL 22 - Thu

### **POLYMER SEMICONDUCTOR SOLAR CELLS – DESIGN OF STRUCTURES FOR CHARGE PHOTOGENERATION, SEPARATION AND COLLECTION**

R H Friend

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Conjugated polymers are now well established as useful semiconducting materials, allowing both convenient processing, usually from solution, together with a range of electronic properties that support operation of light-emitting diodes, LEDs, field-effect transistors, FETs, and photovoltaic diodes, PVs. The very substantial improvements over the past few years in all aspects of device performance (LED and PV efficiency, FET mobility) have been achieved principally through the control of polymer structure, both in bulk, and more particularly, at heterointerfaces. Semiconductor-semiconductor interfaces are critical for the operation of both LEDs and PVs since these are required to control the energetics of charge carrier recombination (LEDs) or separation (PVs). I will illustrate some of the recent progress made in the design and control of both structure and electronic structure in these systems.

## IL 23 - Thu

### POLYMER NANO- AND MICROPARTICLE BASED SYSTEMS FOR MEDICAL DIAGNOSTICS

S.Slomkowski, T.Basinska

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Polymer nano- and microspheres have dimensions usually only from ca 10 to 500 times larger than macromolecules to be detected (often proteins or nucleic acids). On the other hand, they can be easily observed using a variety of well known analytical methods (e.g. by light scattering). Thus, nano- and microparticles with immobilized biomolecules, that are able for binding specifically selected molecules, can be used as convenient tools for detection of the latter [1-4]. Nano- and microparticles with immobilized enzymes can be used for detection of particular substrates in analyzed mixtures. For all applications are needed particles binding biomolecules in a highly specific manner, without unwanted adventitious adsorption. In the lecture we will describe syntheses of polymer particles with aldehyde, carboxyl and hydroxyl functions. Properties of these particles, in particular their ability of covalent immobilization of proteins with eliminated or at least reduced nonspecific adsorption of proteins from analyzed body fluids will be discussed.

In multisensing elements there are needed assemblies of particles with different size and surface properties. Our attention will be concentrated on assemblies formed from two sets of particles that are chemically identical and have narrow diameter dispersity within a set but between sets differ with respect to their diameters.

Examples of classical and of so-called “dry tests” based on polymer microspheres as well as of optrodes for biosensors with optical detection that are made from microspheres will be presented. There will be described also a new class of diagnostic tests based on monitoring changes of electrophoretic mobility of microspheres exposed to contact with appropriate analyte as well as diagnostic tests based on properties of colloidal photonic crystals [5-6].

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# IL 24 - Thu

## THIN FUNCTIONAL POLYMER FILMS FOR MICRO- AND NANOPATTERNING

B. Voit<sup>1</sup>, F. Braun<sup>1</sup>, S. Fleischmann, M. Millaruelo Boira<sup>1</sup>, M. Messerschmidt<sup>1</sup>, J. Stadermann, M. Mertig<sup>2</sup>,

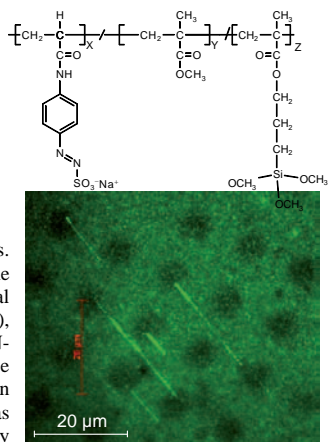
<sup>1</sup>Leibniz Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany, [voit@ipfdd.de](mailto:voit@ipfdd.de); <sup>2</sup>Technische Universität Dresden, Institut für Werkstoffwissenschaft und Max Bergmann Zentrum für Biomaterialien

The present high-tech era requires more and more faster and smaller elements and systems, e.g., in microelectronics, sensors, or medicine. Common imaging technologies for structuring have now reached their limits, therefore novel technologies are necessary to obtain structure dimensions and functional elements on a nano or even molecular scale. Today metallization and surface finishing are important fields of applications in our macroscopic world as well in nanotechnology. Selforganization and phase separation of functional block copolymers is one approach to pattern thin organic films. Another point of interest is the spatially defined provision of functional groups as docking stations for the defined attachment of functional elements like molecular switches or carbon nanotubes to build – in future – nanomachines or at least microreactors containing nanoelements.

We would like to report the successful selective metal deposition using photolabile polymer consisting of a diazosulfonate side chain groups. In addition to 20 mol% diazosulfonate monomer the terpolymer contains 5 mol% of a silane compound, which is necessary for the covalent anchoring of the film onto the substrate.

Furthermore, films were preparation of photolabile protected low molar mass and polymeric amines on glass and silicon substrates. These films are suitable for imagewise structuring by UV-light and laser irradiation and nanoelements like DNA strands could be attached individually in further steps. These polymeric amines with similar structure like the diazosulfonate terpolymers were synthesized by radical polymerization of three monomer units which are MMA (spacer), 3-(trimethoxysilyl) propylmethacrylate (anchoring group) and N-(N-VOOC-aminopropyl)-methacryl-amide (photolabile compound). The anchoring groups were varied to allow also thin film preparation e.g. on gold substrates. The functionality was varied from azosulfonate and labile sulfonate esters, to differently protected amines to labile protected carboxylic acids. Selective deprotection by heat or light could be varied.

Finally various functional block copolymers were prepared by controlled radical polymerization. Highly ordered nanostructures could be realized in thin films of these polymers. Again, functionalities which on the one hand allow surface anchorage, and on the other hand are suitable for patterning with functionalities e.g. by light, are introduced in those block copolymers which offers the chance to combine the bottom-up approach through phase separation with typical top-down lithographic patterning.



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## IL 25 - Thu

### HYDROGEN ECONOMY AND POLYMERIC MEMBRANES

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Hydrogen is intended to be an important energy carrier in the sustainable energy future. Today the steam reforming of fossil fuels is the most employed method for hydrogen production but this way does not meet the demand for renewable sources and brings various environmental problems. The methods that meet modern ecological criteria are the electrolysis of water and fermentation processes.

Electrolysis of water produces hydrogen of the highest quality. It can be powered by totally renewable energy sources, such as wind and solar energy. In most of the commercial electrolyzers, asbestos is used as diaphragm and concentrated aqueous KOH as an electrolyte. Future electrolyzers with ion-exchange membranes will not use harmful asbestos and will allow to decrease considerably the concentration of dangerous and corrosive electrolytes. One important part of the present research is focused on the development of highly conductive and stable ion exchange membranes.

Biological methods of hydrogen production represent promising renewable sources of energy. They are based on activities of some photoautotrophic and anaerobic heterotrophic microorganisms. The gas mixture formed during fermentation contains the product, hydrogen, quite diluted. Nonporous composite membranes, formed as hollow fibers, are very suitable for hydrogen separation. Polymeric foams with closed cells can serve for separation and storage of hydrogen as well.

Hydrogen produced can be stored and used later to produce energy in fuel cells giving back water, in an environmentally clean process. A vital part of the fuel cells is a membrane which must be proton conductive.

# IL 26 - Thu

## **BIOSTABLE AND BIODEGRADABLE METHACRYLATE HYDROGELS FOR HEALING AND TISSUE REGENERATION**

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Poly(2-hydroxyethyl methacrylate)(pHEMA) crosslinked hydrogels have been explored for medical and dental applications for almost 50 years. They are remarkably biostable. Given the excellent *in vivo* safety of this polymer, it would be desirable to have it in a biodegradable form for tissue engineering scaffolds and drug delivery.

To achieve biodegradability in pHEMA, we ensure that all chains are 6000 Da or less – these short chains are water soluble, non-toxic to cells and can be cleared through the kidneys. The molecular weight of the pHEMA chains is controlled using atom transfer radical polymerization (ATRP). To achieve good mechanical properties, a degradable polycaprolactone (PCL) macroinitiator will be used to increase initial chain length to twice the clearance limit (10K-12K Da) while allowing for soluble degradation products. Tuning of the pHEMA hydrogel degradation depends on the hydrolytically labile crosslinking regions. Modulating degradation rate is achieved by varying the number of degradable units or the rate at which they are cleaved via water access to the site. A number of degradable block chemistries have been explored. Degradation is first observed by a swelling of the polymer and then by mass loss.

A special focus in this talk will be on unique porous materials made by sphere templating that rapidly induces angiogenesis and minimizes fibrotic outcomes. Biocompatibility data will be presented. A special variant of this material will have long, parallel pores for heart muscle cells and spherical pores to induce angiogenesis.

## IL 27 - Thu

### BIOHYBRID HYDROGELS FOR REGENERATIVE THERAPIES

U. Freudenberg, P.B. Welzel, K. Levental, A. Zieris, W. Panyanuwat, M. Grimmer, C. Werner

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With the advent of regenerative therapies morphogenetic matrices capable of rekindling the cellular potential to regenerate tissues and organs evolve into a new paradigm of biomaterials research: Advanced therapeutic concepts require biodegradable cell scaffolds transmitting spatio-temporal sequences of signals to trigger cellular fate decisions. - Control over biomolecular complexity *and* mechanical characteristics of biofunctional matrices are expected to open new options for *in vivo* tissue engineering strategies [1,2].

To address this challenge, we report a modular system of biohybrid hydrogels based on heparin and synthetic star-shaped poly(ethylene glycols) (star-PEG). As a key feature, our system permits to gradually vary the network characteristics at constant heparin contents. The secondary conversion of the heparin component of the biohybrid materials was demonstrated to allow for the covalent attachment of cell adhesion mediating RGD-peptides and the non-covalent binding of the soluble proliferation factor/mitogen FGF-2. Ongoing work is now focused on heparin-starPEG hydrogels crosslinked by matrix metalloproteinase (MMP) sensitive peptides allowing for the enzyme controlled remodeling of the matrix by invading cells.

The novel biohybrid materials are applied to explore the interplay of biomolecular and mechanical stimuli in cellular fate decisions. Beyond that, the hydrogels support cell replacement and regeneration strategies in various therapeutic approaches for neurodegenerative diseases.

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# SL 1 - Mon

## **POROUS BIODEGRADABLE POLYMERS AND HYDROGELS THROUGH EMULSION TEMPLATING**

M.S. Silverstein

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Porous biodegradable and hydrogel polymer systems synthesized through emulsion templating within high internal phase emulsions (HIPE), polyHIPE, could be of interest for drug delivery and tissue engineering applications. A vinyl terminated polycaprolactone oligomer was used as a crosslinking comonomer for the synthesis of both stiff and elastomeric polyHIPE scaffolds. The degradation of the scaffold and cell growth within the scaffold were strongly dependent upon the nature of the system. Bicontinuous systems consisting of polyacrylamide-based hydrogels in the internal phase and hydrophobic polymers in the external phase were also synthesized within HIPE. Although the external phase of the HIPE remained unchanged, the properties of the bicontinuous polyHIPE changed with the acrylamide content in the internal phase, indicating that the polymerization reactions were not mutually exclusive.

## SL 2 - Mon

### PREPARATION OF MACROPOROUS POLY (ACRYLAMIDE) HYDROGELS IN DMSO/ WATER MIXTURE

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Synthesis of hydrogels exhibiting fast response rate to the external stimuli is a requirement in many application areas of these materials. A widely used approach to obtain fast-responsive hydrogels is to create voids (pores) inside the hydrogel matrix, so that the response rate becomes a function of the microstructure rather than the size or the shape of the gel samples. There are two basic techniques to obtain hydrogels with a macroporous structure. The first technique, called reaction-induced phase separation, involves the free-radical crosslinking copolymerization of the monomer-crosslinker mixture in the presence of an inert diluent, which is soluble in the monomer mixture [1]. In order to obtain macroporous structures, a phase separation must occur during the course of the gelation process so that the two-phase structure formed is fixed by the formation of additional crosslinks. After the polymerization, the diluent is removed from the network, leaving a porous structure within the highly crosslinked polymer network. Another technique is the cryogelation where the polymer formation reactions are carried out below the bulk freezing temperature of the reaction system [2]. Thus, the essential feature of such reaction systems is that the monomers and the initiator are concentrated in the unfrozen microzones of the apparently frozen system. The polymerization and crosslinking reactions proceed in the unfrozen microzones of the reaction system. A macroporous structure in the final material appears due to the existence of ice crystals acting as a template for the formation of the pores [3].

In this study, we describe, for the first time based on our knowledge, the change of the formation mechanism of the porous structures in hydrogels from cryogelation to phase separation polymerization by simply varying an experimental parameter. By conducting the crosslinking polymerization of acrylamide in aqueous DMSO solutions, we were able to manipulate the porosity formation mechanism through the amount of DMSO present in the reaction system.

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## SL 3 - Wed

### TRANSPARENT UV-ABSORBING PMMA/ZnO NANOCOMPOSITES

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The polymer nanocomposites are known to possess different or enhanced properties as compared to pure polymers, which is the consequence of the large specific surface area of nanoparticles leading to enhanced interfacial reactions between them and the polymer matrix. Zinc(II) oxide, ZnO, is a wide band gap (3.37 eV) semiconductor and this makes it an excellent UV absorber. On the other hand, poly(methyl methacrylate), PMMA, is a thermoplastic material with exceptional optical and favourable mechanical properties making this material suitable for many applications. Transparent PMMA/ZnO nanocomposites with high UV absorption are obtained when ZnO of dimensions below 100 nm is employed, which, in addition, thermally stabilizes the PMMA matrix. For the preparation of homogeneous ZnO/PMMA nanocomposites it is crucial to achieve good dispersion stability, usually by using surface-functionalized ZnO nanoparticles.

We synthesized ZnO nanoparticles (NP) by the polyol method using various diols and p-toluene sulphonic acid (p-TSA) as a capping agent. By this method the ZnO NP with organophilic surface were prepared meaning that no additional surface modification was needed. The average particle size varied from 20 to 100 nm depending on the diol used. PMMA/ZnO nanocomposites were synthesized by the *in situ* polymerization of MMA monomer in bulk.

ZnO NP are extremely efficient UV absorber since PMMA plates with 3.5 mm thickness and 0.1 wt.% of ZnO absorbed more than 98 % of the incident UV light. The addition of 1 wt.% ZnO NP into PMMA matrix shifted the thermal degradation onset for 40 °C towards higher temperatures. This phenomenon was explained by the active role of ZnO NP in the termination of polymerization. In addition, they increased the polymerization reaction rate, reduced the polymerization activation energy, and increased the PMMA molar mass average. These effects are strongly related to the average particle size of ZnO: the lower the particle size, the more effective are ZnO NP. By optimising the nanocomposite preparation procedure transparent PMMA/ZnO sheets were prepared having high potential for applications as thermally and UV stabilized PMMA plates or protective films.

## SL 4 - Wed

### **BIOBASED POLYURETHANE NANOCOMPOSITE FOAM**

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The synthesis of PU nanocomposite foams from bio-based polyols obtained from vegetable oil will be discussed. Different types of nanoclays was used to enhance the performance of the foams. The behaviour and properties of the obtained nanocomposite foams were characterized by different means including FTIR, DSC, DMTA, TGA-DTA, and mechanical testing such as compression and flexion at different conditions. The results demonstrate the bio-foams have comparable properties as the petroleum-based foams.

## SL 5 - Wed

### IRRADIATED MICROWAVE SYNTHESIS: A NEW WAY TO OBTAIN CONDUCTING COPOLYMERS

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Microwave (MW) synthesis represents a major breakthrough in synthetic chemistry versus conventional heating sometimes known to be time consuming because of its low efficiency. If the microwave energy was developed for industrial application from the middle of the 20<sup>th</sup> century, first microwave-enhanced organic chemistry was not explored until the mid 1980s. In comparison to the impressive development of the microwave technique in organic synthesis during the last decades, microwave-assisted polymer synthesis is rather new emerging field and mainly reported from the late of 1990's (1;2;3). The synthesis of block copolymers containing one block of intrinsic conducting polymer (4) has already been reported. The strategies involved fastidious synthesis as multi-step syntheses and drastic experimental conditions. However the synthesis of these kind of polymer are still of interest because these materials are used as models to study the conduction phenomena and interface organization (4), may be used as conducting additives in insulating matrices (5).

The aim of our work is to study the use of MW synthesis to obtain conducting block copolymers while controlling the molecular weights and polydispersity. The objectives are at the same time to reduce the duration of the synthesis while keeping the process as simple as possible. Special attention is also given to the comparison with the results obtained under conventional heating to determine the occurrence of non-thermal microwave effects which is still a controversial topic.

After a brief presentation of the MW irradiation methods *i.e.* dynamic and pulsed modes, kinetic results will be presented and evidence of living/controlled nature of the polymer will be given. The occurrence of a "microwave effect" will be discussed. The block copolymers containing a conducting block of poly- or oligo-aniline were characterized to confirm their morphology and intrinsic properties.

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# SL 6 - Wed

## STUDIES ON THE EFFECTS OF ARGININE RESIDUES INTRODUCED TO PEPTIDE RIBONUCLEIC ACIDS (PRNA) ON THE COMPLEX STABILITY WITH RNA AND THE CELL MEMBRANE PERMEABILITY

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We have reported the effect of adding borax on the nucleobase orientation and recognition behavior of novel oligomeric  $\alpha$ - and  $\gamma$ -peptide ribonucleic acids ( $\alpha$ - and  $\gamma$ -PRNAs).<sup>1</sup> The base orientation of 5'-aminopyrimidine ribonucleosides in recognition moieties of PRNAs were shown by CD and NOE difference spectral studies to switch from *anti* to *syn* upon addition of borax. The origin of this phenomenon is elucidated to be the cooperative effect of the cyclic borate esterification of the ribose's *cis*-2',3'-diol and the hydrogen-bonding interaction between the ribose's 5'-amino proton and the base's 2-carbonyl oxygen. Therefore, it was unambiguously demonstrated that  $\gamma$ -PRNAs with an isopropyl(L-glutamic acid) backbone can form a stable complex with DNA and further the recognition of DNA with  $\gamma$ -PRNAs is controlled by the borate added as an external factor. Nevertheless, the transfection efficiency of not only natural and modified DNA, but also artificial nucleic acids possessing amide backbones, such as PNA is often not satisfactory, primarily due to the low permeability of the molecules through cell membrane.<sup>2</sup> In the meantime, active cellular-uptake using membrane-permeable peptide vectors is a recently developed methodology. The efficient delivery of proteins and nucleic acids using the method by conjugating with basic peptide segments, such as arginine-rich peptides has been reported.<sup>2</sup> Thus, in this paper, we have designed and synthesized a series of  $\alpha$ -PRNAs possessing alternative  $\alpha$ -PRNA/lysine and  $\alpha$ -PRNA/arginine sequences (Chart 1).

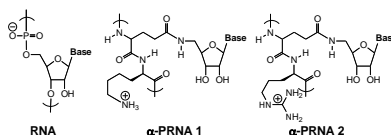


Chart 1. Structure of RNA and  $\alpha$ -PRNAs.

**Synthesis of  $\alpha$ -PRNAs.**  $\alpha$ -PRNA **1**, and  $\alpha$ -PRNA **2** are synthesized by a Fmoc-solid phase peptide synthesis.<sup>3</sup> The PRNA oligomers obtained were purified by reversed phase preparative HPLC.

### CD Spectral Study on $\alpha$ -PRNA Oligomers.

**Table 1.** Melting temperatures ( $T_m$ ) of  $\alpha$ -PRNA **1** and **2** with oligonucleotide complexes

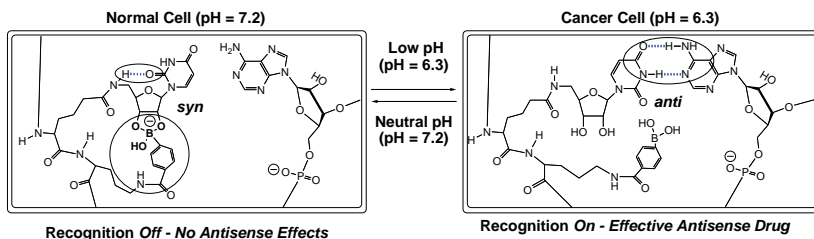
PRNA or DNA	complement	$T_m$ / °C	
		borax /mM	
		0	20
$\alpha$ -PRNA <b>1</b> (UKUKUKUKUKUKUKUK)	d(A) <sub>8</sub>	25	< 2
$\alpha$ -PRNA <b>2</b> (URURURURURURURUK)		40	< 2
	d(T) <sub>8</sub>	2	5

[PRNA] = [Oligonucleotide] =  $1.0 \times 10^{-5}$  M (1 / 3000 M phosphate buffer, pH 7.0)

The CD spectra were measured at various concentrations of borax added to a phosphate buffer solution of  $\alpha$ -PRNA **8**-mers (**1** and **2**). In phosphate buffer, the  $[\theta]_{\text{ext}}$  value of  $\alpha$ -PRNA **1** obtained ( $6500 \text{ deg cm}^2 \text{ dmol}^{-1}$ ) was nearly the same as that observed for 5'-amino-5'-dexoyridine, and this is compatible with the preferred *anti* orientation in phosphate buffer.<sup>1</sup> The CD intensity continuously decreased as the concentration of borax increased, leveling off between 1.9 and 5 mM. The CD spectra observed at borax concentrations of borax >1.9 mM is almost superimposable upon that obtained in borate buffer, which contains 20 mM of borax. The gradual CD spectral changes, accompanied by the isosbestic points observed at *ca.* 230 and 250 nm, indicate clearly that the reversible *anti*-to-*syn* orientation switching process is caused by a cooperative cyclic borate

ester formation and hydrogen bonding interaction, as observed for the 5'-aminouridine and the  $\gamma$ -PRNA oligomers.' A quantitative treatment of these CD spectral changes of  $\alpha$ -PRNA **1**, using the non-linear least squares fitting to the curve for 1:1 stoichiometric complexation, gave the equilibrium constant of  $3000 \text{ M}^{-1}$  for the formation of borate ester for each ribonucleoside, which is exactly 40 times greater than that obtained for 5'-aminouridine under the comparable conditions.

**Control of Hybridization of  $\alpha$ -PRNA with Complementary DNA by Borate Ester Formation.** The hybridization ability of  $\alpha$ -PRNA **1** and **2** with complementary d(A)<sub>8</sub> was evaluated from the melting temperature,  $T_m$ . In order to elucidate the effects of borate on the formation and stability of the  $\alpha$ -PRNA-DNA hybrid, the melting profiles for the  $\alpha$ -PRNA **1** and **2** pairs and the reference compound d(T)<sub>8</sub> with the complementary d(A)<sub>8</sub> were measured independently in phosphate buffer with and without borax (20 mM). Table 1 summarizes the  $T_m$  values observed. The stoichiometry of the complex with d(A)<sub>8</sub> was determined to be 1:1 in each case (uracil or



**Scheme 1.** Recognition and complexation behavior control of  $\alpha$ -PRNA1-RNA.

thymine: adenine unit ratio) using the Job plot of the hypochromic change upon mixing. Control runs using non-complementary d(T)<sub>8</sub> in place of d(A)<sub>8</sub> were also carried out under compatible conditions and found to show no hypochromicity or appreciable melting behavior. This confirms the base-specific interaction of  $\alpha$ -PRNA **1** and **2** with the complementary d(A)<sub>8</sub>, and then also indicates that an inconsiderable contribution of a non-specific electrostatic interaction between basic amino residues of  $\alpha$ -PRNA **1** and **2** and phosphate backbone of DNA's in the  $\alpha$ -PRNA – DNA complexes.

As shown in Table 1, in borax-free buffer, the hybrid complex between  $\alpha$ -PRNA **1** and d(A)<sub>8</sub> gave a considerably higher  $T_m$  of  $25.0 \text{ }^\circ\text{C}$  than the complementary d(T)<sub>8</sub>-d(A)<sub>8</sub> duplex ( $T_m = 2.0 \text{ }^\circ\text{C}$ ) under the same condition, indicating a stronger interaction in the hybrid than in the natural pair. The complexation behavior of  $\alpha$ -PRNA **2**, which possesses alternating uridine PRNA monomer and arginine residue, was studied under the same condition. The  $\alpha$ -PRNA **2** complex with d(A)<sub>8</sub> gives a  $T_m$  of  $40.0 \text{ }^\circ\text{C}$  with hypochromicity of 50%, which is appreciably higher than that obtained for the  $\alpha$ -PRNA **1**-DNA complex. This result may indicate that a guanidium cation group of arginine residue of  $\alpha$ -PRNA **2** efficiently binds to target DNA phosphate anions on the backbone, rather than that of an ammonium group of lysine residue of  $\alpha$ -PRNA **1**, although the non-specific electrostatic interaction between cationic residues of  $\alpha$ -PRNA and negatively charged DNA backbone would be negligible.

In contrast, in the borax-containing buffer solution, the hybrid complex of  $\alpha$ -PRNA **1** and **2** with d(A)<sub>8</sub> did not exhibit any melting behavior above  $2 \text{ }^\circ\text{C}$ , or hypochromic changes, while the complementary (T)<sub>8</sub>-d(A)<sub>8</sub> duplex gave an appreciably higher  $T_m$  of  $5.0 \text{ }^\circ\text{C}$ , presumably due to the slight increase in the ionic strength. This contrasting behavior between the natural and PRNA hybrid pairs in the presence/absence of borax is most likely attributable to the *anti*-to-*syn* orientation switching of the uracil base in  $\alpha$ -PRNA, for which a cooperative borate ester formation at the *cis*-2',3'-diol and a hydrogen bonding interaction between the 5'-amide proton and the 2-carbonyl oxygen are responsible. However, the electrostatic repulsion between the adjacent anionic borate esters makes some contribution, as illustrated in Scheme 1.

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## SL 7 - Wed

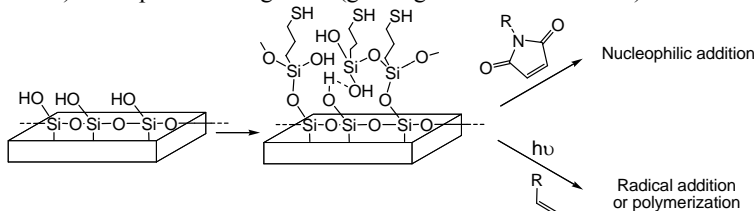
### THIOL-ENE CHEMISTRY ON GLASS SLIDES: EASY WAY TO CARBOHYDRATE MICROARRAYS, PROTEIN RECOGNITION, AND TUNABLE SURFACES

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This work highlights the simplicity of a thiol-derivatized glass surface as a tool for tuning its chemical surface (polymers, sugars, biotin ...) by thiol-ene photochemistry.

To prepare robust layers on glass slides, covalent stabilization is often employed by means of organo-siloxanes<sup>[1]</sup> which can further be used to trigger surface-initiated polymerizations.<sup>[2]</sup> Especially, surface bonded thiols are of great importance, as they can be used for a “grafting onto” approach by means of thiol-ene chemistry as well as a “grafting from” approach by initiating polymerization. Herein, we report a metal catalyst-free approach (on the contrary to Huisgen-type click chemistry), generalized functionalization of glass slides, by means of orthogonal reactions: light initiated “thiol-ene” chemistry and nucleophilic addition (see Scheme 1), which can find applications in materials science (grafting of olefins), development of carbohydrate microarrays (grafting of glucose derivatives)<sup>[3]</sup> and protein recognition (grafting of biotin-maleimide).<sup>[4]</sup>



**Scheme 1.** Scheme of the reaction procedures of ene-reagents on a thiolated glass slide surface through radical addition and nucleophilic addition.

**Acknowledgment.** Financial support was given by the BMBF in the framework of a “Bionik-Initiative” (0313765A).

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## SL 8 - Wed

### **PROPERTIES OF POLYMERIC SURFACES SUITABLE FOR LINKER FREE COVALENT BINDING OF FUNCTIONAL BIOMOLECULES: THE ROLE OF FREE RADICALS**

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In previous work [1-4], we have demonstrated two processes for the preparation of polymer-like surfaces which are capable of covalently immobilising a dense monolayer of proteins directly upon incubation in a protein-containing buffer solution. Both processes rely on the use of energetic ions: in the first case they are implanted into a polymer surface; while in the second process they are used to treat a growing plasma polymer which can be successfully adhered to any underlying material. The surfaces created in both ways showed very similar protein binding characteristics. They were conducive to long lived bioactivity of immobilised biomolecules both in solution and after freeze drying and showed long shelf times prior to the protein attachment.

In this paper, we will present information on the structure and properties of these surfaces and attempt to link them to aspects of the favourable protein immobilisation characteristics. We present also substantial evidence for a role of mobile free radicals in the covalent immobilisation process and will conclude with our model for describing the linker free covalent binding mechanism.

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## SL 9 - Thu

### **SUPRAMOLECULAR STRUCTURE FORMATION: WHAT IS THE PHYSICAL BASIS?**

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Supra-molecular structures are essential elements in biological systems. They are formed due to mutual interactions among the particles. In addition higher organized organelles i.e. assemblies of functional properties, can be built up. A check of observed supra-molecular structures revealed two main types, One is based on spherical shapes (micelles and vesicles), the other on rod-like topologies.

Selected examples are discussed. In several cases the reason for stability could be made intelligible. Besides a specific topology the confinement in semi-dilute solution has a decisive influence. In other examples the physical basis remained not evident. An attempt is made to close gaps in our understanding which is considered to be essential for a sensible design of organelles with desired specific properties.



# P 1 - Mon

## INTERMOLECULAR INTERACTIONS AND STRUCTURE OF WATER IN POLY(VINYL METHYL ETHER) HYDROGELS

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Amazing properties of polymer stimuli-responsive hydrogels for which they find numerous applications in medicine, pharmacy and cosmetics are mostly a result of polymer-water and water-water interactions. Volume phase transition observed in this class of material and triggered by very small changes in external conditions (e.g.: pH, temperature, electromagnetic field) is usually related to loss of balance in intermolecular interactions.

In presented work intermolecular interactions were analyzed in series of poly(vinyl methyl ether) (PVME) hydrogels crosslinked by electron-beam irradiation. Applied doses in the range 13-65 kGy resulted in various crosslinking degrees. Analysis of polymer  $\nu(\text{CH}_3)$  and  $\nu(\text{CH}_2)$  stretching vibrations in Raman spectra has allowed to monitor the changes of hydrophilic and hydrophobic polymer-water interactions in a course of water deswelling and volume phase transition. Formation of water-polymer hydrogen bonds has appeared to influence directly supramolecular structure of the absorbed water. It was found that the polymer network density determines an availability of the hydrophilic sites to water molecules and also influences the kinetics of volume phase transition of the hydrogels. Activation energy of the polymer conformational changes related to volume phase transition was estimated to be ca. 88 kJ/mol.

### Acknowledgements

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## P 2 - Mon

### ARTIFICIAL FIBRIN GELS FOR BLOOD VESSEL ENGINEERING

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When exposed to blood, any surface other than that of undamaged vascular wall endothelium induces blood coagulation. Fibrin network formed after injury to stop bleeding, later, serves as a temporary scaffold for cells repairing the damaged vessel. These processes help organism to maintain haemostasis after vessel injury, however, they are a source of troubles when synthetic materials are used in cardio-vascular surgery. Particularly, small diameter vessel grafts displayed high failure ratios due to thrombus formation and perianastomotic hyperplasia. A confluent, semipermeable layer of endothelial cells (EC) grown in vitro on the inner side of grafts can solve the problems.

In this work, knitted polyethylene terephthalate (PET) vascular prostheses modified with collagen were coated with artificial fibrin gels using a novel technique based on the catalytic activity of surface-bound thrombin on fibrinogen solution. Thin fibrin networks were formed on surface of polymer fibers without filling the space between them with bulk fibrin gel when antithrombin III was used for inhibition thrombin released into solution. A confluent layer of bovine pulmonary artery endothelial cells formed on the fibrin coated prostheses after 7 days in vitro cultivation. The technique makes it possible to encourage the endothelization vascular prosthesis lumen while preserving the free space in the vessel wall for potential capillary vascularization.

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## P 3 - Mon

### **COMPARISON OF THE PROPERTIES OF NOVEL MATERIALS BASED ON COLLAGEN, CHITOSAN AND HYDROXYAPATITE**

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Reconstruction of bone defects caused by trauma or surgical operation of a bone tumor is a major issue in orthopedic surgery. Bone is an inorganic-bioorganic composite material consisting mainly of nano-sized hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAp) and collagen fibers (Col). Synthetic HAp has excellent biocompatibility and bioactivity due to its chemical and structural resemblance to mineral bone and tooth. However the application of pure HAp is very limited due to its brittleness. Thus, composite materials made from HAp and a biopolymer like collagen and/or chitosan can be applied in bone tissue regeneration. The blends of collagen with HAp and chitosan with HAp have been studied by our research group. The aim of the work was to study and compare the properties of collagen/HAp and chitosan/HAp films.

Collagen was obtained in our laboratory from tail tendons of young albino rats. Hydroxyapatite (nanopowder) and chitosan were supplied by the company of Sigma-Aldrich. Polymeric blends with HAp were prepared by mixing suitable volumes of collagen, chitosan and nano-powder of HAp. Polymer films were obtained by solution casting onto glass plates. After solvent evaporation, the specimens were dried at room temperature. The properties of collagen/HAp and chitosan/HAp thin films were studied by attenuated total reflection infrared spectroscopy (FTIR-ATR), Scanning Electron Microscopy (SEM) and Energy-dispersive X-Ray Spectroscopy (EDX).

The results have shown that microstructure, especially distribution of phosphate groups and calcium ions on the surface of the blend depends on the specimen's composition.

#### **ACKNOWLEDGEMENTS**

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## P 4 - Mon

### **HONEYCOMB-PATTERNED TOPOGRAPHY REGULATES CELL SHAPE AND IMPROVES PROLIFERATIVE ABILITY OF MULTIPOTENT ADULT STEM CELLS**

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Adult stem cells are able to self-replicate and differentiate into a various major specialized cell types of tissues or organs. They secrete angiogenesis factor and activating factor for damaged cells. Thus, adult stem cells seem to be an appealing therapeutic tool for cell transplantation and tissue engineering. Adult stem cells are thought to reside at low frequency in a special area of tissues or organs (called a „stem cell niche“) so that they need to be expanded *in vitro* to secure sufficient cell numbers required for tissue repair. However, adult stem cells show a short proliferative longevity and easily lose the differentiation potential in culture. Thus, improving their replicative ability is important challenge for the practical application of the cellular therapy.

Polymeric substrates with micrometer to nanometer scale features are currently in use to investigate the reaction of cells to surface topography. In order to address the question if the proliferation ability of adult stem cells is able to be enhanced by surface topology, here, mesenchymal stem cells (MSCs) from rat bone marrow and neural stem / progenitor cells (NSCs) from the cerebral cortex of embryonic 14 day mice were cultured on 3D-double layer polymeric scaffolds equipped with honeycomb patterned micropores („Honeycomb films“) prepared by casting a polymer solution of water-immiscible solvent under high humidity. We found that the proliferative ability was sensitive to the honeycomb-patterned topography with regard to the pore diameter in a way that influences cell shape, and in turn, cell proliferation and was higher than that of both on a control flat film and commercially available tissue culture plate (TC). The cellular shape of MSCs on a 1  $\mu\text{m}$  pore polystyrene honeycomb films was round but spread flat on the films with the pore size larger than 5  $\mu\text{m}$ . Smaller the pore size, higher their proliferative ability. The proliferative ability on a 1  $\mu\text{m}$  pore film was higher than that on polystyrene TC. NSCs on poly ( $\epsilon$ -caprolactone) honeycomb films with pore sizes other than 3  $\mu\text{m}$  differentiated into neurons. Interestingly, NSCs self-replicated specifically on a 3  $\mu\text{m}$  pore honeycomb film and formed spheroids. In addition, some NSCs resided undifferentiated state: They neither differentiated nor proliferated, suggesting that the 3  $\mu\text{m}$  honeycomb film acts as „a stem cell niche „for NSCs. The results suggested that the honeycomb film is a potential scaffold improving proliferative ability of adult stem cells and serving as their niche.

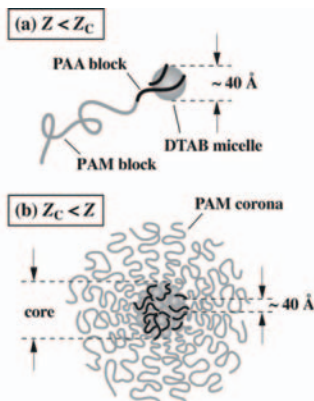
## P 5 – Mon

### ELECTROSTATIC SELF-ASSEMBLY OF CHARGED BLOCK COPOLYMERS AND LOW MOLECULAR-WEIGHT MOLECULES

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Complexes involving oppositely charged polyelectrolyte or polyelectrolyte and low-molecular-weight surfactant constitute a very active field of research in recent years. These systems also show similarities in structure and behavior with more complex biological macromolecular self-assembled systems, such as lipoproteins, and protein/DNA complexes. The overall size and the stability of the colloid depend on the electrostatic charges, on the molecular weight, and on the flexibility of the chains. In this study, we investigate the structure and the stability of the colloidal complexes obtained from poly(acrylamide)-*block*-poly(acrylic acid) (PAM-*b*-PAA) and dodecyl trimethylammonium bromide (DTAB) as oppositely charged surfactant by dynamic light scattering and small-angle neutron scattering. When a surfactant-to-polymer charge ratio  $Z$  is lower than the critical value  $Z_C$ , the colloidal complexes are single DTAB micelles dressed by a few PAM-*b*-PAA (Fig. 1a). Above  $Z_C$ , the colloidal complexes form a core-shell microstructure. The core of the complex consists of densely packed surfactant micelles (DTA<sup>+</sup>), and PAA block chains bind to these micelles, displace their counteranions (Br<sup>-</sup>) and bridge them together (Fig. 1b). The corona of the complex is a diffuse shell of PAM chains and it ensures steric stability. Since the interaction is primarily electrostatic in nature, the addition of salt should have a significant effect on the complex formation. The salt-enhancing effect on the complex formation is observed in the PAM-*b*-PAA/DTAB system; the critical surfactant concentration decreases with increasing salt concentration. The salt-enhancing effect is due to the larger increasing of interaction in comparison with the screening of interaction. At higher salt concentration, higher electrostatic inter-micellar repulsion and inter-complex repulsion lead to a redissolution of large complexes into small complexes.



**Fig. 1** Schematic representation of (a) DTA<sup>+</sup> micelle decorated by PAM-*b*-PAA ( $Z < Z_C$ ), and (b) a colloidal complex formed by association of PAM-*b*-PAA and DTAB ( $Z_C < Z$ ).

## P 6 - Mon

### NEW HYDROGEL SUPPORT FOR CELL CULTURES FOR MEDICAL AND RESEARCH PURPOSES

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The cell therapy represents new, rapidly progressing discipline of biomedical research where cultured keratinocytes were the very first cells used in clinical scale. This topic is in the center of our interest when grafting of cultured keratinocytes with their cultivation support represents procedure that was successful under the preliminary clinical trials. Adhesion and spreading represents a necessary condition for successful cultivation of eukaryotic cells. It is realized through cell surface receptors which recognize counterparts such as peptides, proteins or carbohydrates.

The aim of this study is to prepare a universal bioactive cultivation support that would enable the tailor made cultivation of distinct cell types. For controlled immobilization of bioactive motifs, we have chosen a reaction complex avidin-biotin. Appropriate ligand suitable for cell surface receptors is incorporated to the polymer structure by the reaction of its biotinylated form with avidin present on the polymer surface.

As cultivation supports, hydrogels based on 2-ethoxyethyl methacrylate (EOEMA) and glycerol monomethacrylate (GMMA) were prepared by radical crosslinking polymerization. By oxidation of hydroxyl groups present in GMMA using permanganate solution, the carboxyl-enriched polymer surfaces were obtained. Subsequently, carboxylic groups activated by the reaction with *N*-hydroxysuccinimide enabled the covalent attachment of avidin.

Avidin containing hydrogels were tested for keratinocyte cultivation after pretreatment using biotinylated mannose containing neoglycoligands to enhance their adhesion. To evaluate the growth of keratinocytes and characterize their phenotype, MTT metabolic test and immunohistochemical detection of differentiation markers such as keratin 19 were carried out. The results obtained so far show that these hydrogel supports adjusted by biotinylated mannose can improve keratinocyte adhesion and growth and have influence on the differentiation pattern of tested cells.

Acknowledgements: GA AS CR KJB400500902 and MEYS 1M 0538.

## P 7 – Mon

### **POLY(METHYL METHACRYLATE)/ZnO NANOCOMPOSITES BASED ON ORGANOPHILIC ZnO NANORODS**

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ZnO is a widely used semiconductor with an exceptional UV absorption. One-dimensional (1D) nanostructures of ZnO such as nanowires or nanorods have recently attracted a great scientific attention. 1D ZnO nanostructures are very promising materials for applications in microelectronics, sensors, energy storage and conversion, light emitting displays, catalysis, and drug delivery. It is known that many electrical and optical properties of nanomaterials strongly depend on particle size and shape.

ZnO nanorods were synthesized by the hydrolysis of zinc acetate dihydrate in diethylene glycol, DEG, using p-toluene sulphonic acid as an end-capping agent. The dimensions of the prepared ZnO nanorods were 50 – 200 nm in length and 10 – 50 nm in width. XRD diffraction confirmed the presence of crystalline ZnO. Synthesis in DEG gave the nanorods an organophilic character due to the adsorbed diol molecules on the particle surface. For this reason no additional surface modification was needed and we used as-prepared ZnO nanorods for the synthesis of PMMA/ZnO nanocomposites by the *in situ* MMA polymerization in bulk.

ZnO nanorods proved to be highly efficient UV absorber since 1.5 mm thick nanocomposite plates with 0.1 wt.% ZnO absorbed more than 98 % of the incident UV light. The addition of ZnO nanorods also thermally stabilized the PMMA matrix although they were less efficient as compared to the conventional ZnO nanoparticles. By optimizing the nanocomposite preparation the PMMA/ZnO sheets were prepared with high UV absorption (more than 98 % at 0.01 wt. % ZnO) and transparency in the visible spectral region comparable to that of commercial PMMA sheets. The addition of ZnO nanorods also improved the PMMA/ZnO impact resistance by 10 % and substantially enhanced the resistance to sun light (Sun test) giving these materials high potential for various outdoor applications.

## P 8 - Mon

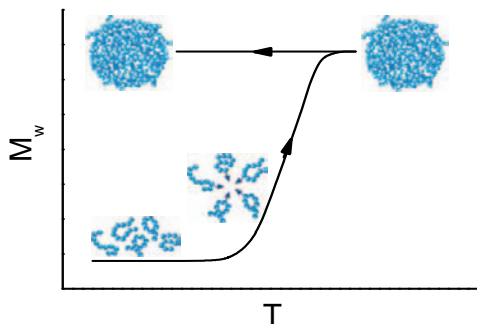
### SELF-ASSEMBLY OF POLY(ETHYLACRYLIC ACID) HOMOPOLYMERS BY HYDROGEN BONDS

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Stable polymeric nanoparticles (complexes) are prepared by self-assembly of poly(ethylacrylic acid) homopolymers (PEA) without any assembly-triggering additives. Nanoparticles are formed in an aqueous solution of thermoresponsive partially charged PEA polymers by hydrophobic interactions on heating towards its lower critical solution temperature (LCST) and subsequently stabilized by hydrogen bonds between polymer chains getting into close proximity. Thermoresponsivity of PEA is tuned by polymer degree of ionization. As a result, stable complexes are obtained which do not change their parameters on cooling. The full irreversibility of the temperature transition is confirmed by scattering methods and by differential scanning calorimetry. Size of complexes can be custom-tailored by tuning critical parameters, especially the temperature and time of heating. Complexes are stable over long periods of time. A deeper insight into the mechanism of the self-assembly is brought by a combination of static, dynamic, and electrophoretic light scattering with calorimetry and FTIR spectroscopy. Nanoparticles stabilized by a concerted action of hydrophobic and hydrogen bond interactions can be denatured by urea similarly to globular proteins.



Scheme of particle formation;  $M_w$  is the weight-average molecular mass.

## P 9 - Mon

### PHOTOELECTRICAL PROPERTIES OF MEH-PPV AND NILE BLUE DYE BLENDS AND BILAYER STRUCTURES

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In searching for suitable organic materials for solar energy harvesting in photovoltaic cells there is a need for materials with efficient optical absorption in the red spectral region. Nile blue (NB) is well known as a strongly absorbing chromophore which exhibits a maximum absorption at 638 nm. It was found that the addition of NB quenches the fluorescence of the semiconductive poly [2-methoxy-5 (2'-ethyl hexyloxy)-1, 4-phenylene vinylene] (MEH-PPV) polymer efficiently. We examined if such quenching appears as a result of an energy transfer or if also charge transfer occurs that leads to increased free charge carrier photogeneration. The blends and bilayer heterojunctions based on polymer MEH-PPV and Nile blue (NB) dye have been fabricated with a structure of ITO/PEDOT:PSS/MEHPPV:NB/Al and ITO/PEDOT:PSS/MEHPPV/NB/Al respectively. The polymer active layers were prepared by spin casting from the solution. In the bilayer structure, NB dye was vacuum deposited on top of the spin coated MEH-PPV film with the deposition rate 0.2 -0.3 nm/s. The effect of dye on the electrical and optical properties of MEH-PPV has been investigated in terms of current-voltage characteristics, optical absorption and fluorescence spectroscopy. NB dye provided significant contribution to the photocurrent due to its strong absorption properties at interface of MEH/NB dye in both the bilayer and blend structures.

## P 10 - Mon

### **POLYANILINE- $\text{Na}^+$ -MMT CLAY NANOCOMPOSITES: SYNTHESIS AND CHARACTERIZATION**

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We demonstrate here a simple, versatile and facile method of obtaining nanocomposites of polyaniline (PANI) and sodium montmorillonite clay ( $\text{Na}^+$ -MMT) using an in-situ intercalative oxidative polymerization of aniline into  $\text{Na}^+$ -MMT. This route offers the possibility to improve the thermal properties with simultaneously keeping a competitive level of the electrical conductivity. The morphology of resulting nanocomposites was characterized by an array of techniques, using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), FTIR, thermo gravimetric analysis (TGA) and electrical conductivity measurements.

X-ray diffraction studies confirm an efficient intercalation of electrically conductive PANI between inorganic clay layers at higher clay loading while at lower loading of clay (2.5 weight %), exfoliation was observed in XRD, which was further confirmed by the SEM and TEM imaging. The interaction between the intercalated PANI and the clay layers was also evidenced by FT-IR spectra. The thermo gravimetric analysis illustrates the improved thermal stability of the intercalated nanocomposites relative to the pure polyaniline due to the incorporation of MMT clay. The electrical conductivity of nanocomposites obtained at room temperature varied from  $2.3 \times 10^{-4}$  to  $7.4 \times 10^{-4} \text{ Scm}^{-1}$  depending on the concentration of the clay and on the experimental conditions employed during the polymerization. We believe that obtaining high thermal stability along with their desired conductivity will be of immense interest in many of our application like EMI shielding material.



# P 11 - Mon

## PREPARATION OF POLYANILINE IN NON-AQUEOUS SOLVENTS

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Polyaniline is one of the most interesting conducting polymers, due to easy way of preparation and excellent environment stability. Polyaniline exists in variety of forms<sup>1</sup>. Protonated form has conductivity on semi-conducting level,  $10 \text{ S cm}^{-1}$ . When polyaniline is deprotonated, the conductivity is at insulator level,  $10^{-9} \text{ S cm}^{-1}$ . The main parameter – conductivity – depends on the way of polymerization. In present case, we have polymerized aniline hydrochloride in non-aqueous media using ammonium peroxydisulfate as oxidant. The nature of the solvent affects the morphology of polyaniline, *e.g.* in acetone polyaniline has a microspherical morphology and in heptane it is amorphous (Figure).

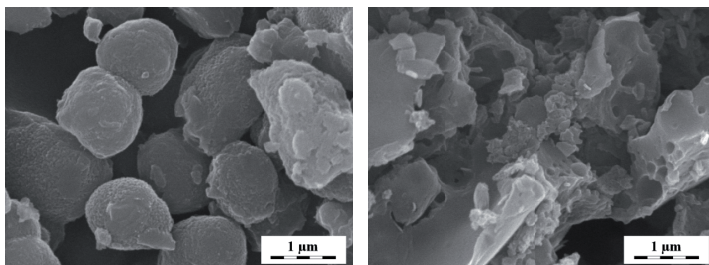


Figure. Polyaniline prepared in acetone (left) and heptane (right).

The novelty of this method consists in the polymerization of aniline in the absence of water, in the suspension of solid reactants. Polyaniline is formed just by mixing solid monomer and oxidant, followed by suspension in a proper organic solvent. Molecular structure of polyaniline was studied by FTIR spectra, conductivity was measured by four-point method, and SEM and TEM were done to see the morphology of polyaniline.

<sup>1</sup> Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E.N. *Macromolecules* **2008**, 41, 3530.

# P 12 - Mon

## NEW PH-TUNABLE BLOCK COPOLYMER NANOPARTICLES VIA CONTROLLED RADICAL POLYMERIZATION AND AZIDE-NITRILE CLICK CHEMISTRY

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Stimuli-responsive polymeric nanoparticles are gaining increasing research interest due to their promising applications in biomedical and diagnostic technology. We have recently explored dilute solution properties and melt phase behavior of high-molecular-weight polystyrene-*block*-poly(styrene-*co*-acrylonitrile) diblock copolymers synthesized by nitroxide-mediated radical polymerization. In addition, it was demonstrated that acrylonitrile units can be efficiently (almost quantitatively) transformed to 5-vinyltetrazole via azide-nitrile click chemistry type post-polymerization modification.

In the current work, nanoparticles consisting of the above diblock polyelectrolytes were prepared by interfacial deposition technique, *i.e.* dissolving diblock copolymer in a common good solvent (DMF) followed by precipitation in the aqueous phase. The hydrodynamic radii  $R_h$  of dialyzed nanoparticles in neutral environment was about 109 nm and the zeta potential -43 mV in NaCl 1mM solution. The pH-response of 5-vinyltetrazole groups was analyzed in a buffer ( $H_3PO_4$ ,  $CH_3COOH$ ,  $H_3BO_3$  and NaOH) spanning pH range from 4 to 10. The dielectric constant was maintained constant by addition of  $NaClO_4$ . The size of nanoparticles obtained by dynamic light scattering was  $R_h = 35$  nm at pH = 4 - 5.5 and was found to increase abruptly by about 3 times around pH = 6.0 - 7.5 to  $R_h = 123$  nm. The latter size remained unchanged within pH range from pH = 7.5 up to pH = 10.

Preliminary results clearly demonstrate the ability of bioactive 5-vinyltetrazole groups to respond to changes in pH-stimulus holding a great opportunity for making smart diblock copolymer nanoparticles for controlled drug delivery.

### Literature:

<sup>1</sup> Gromadzki, D.; Lokaj, J.; Šlouf, M.; Štěpánek, P. *Polymer*, in press

<sup>2</sup> Gromadzki, D.; Lokaj, J.; Černoch, P.; Nallet, F.; Diat, O.; Štěpánek, P. *Eur Polym J*, 44 (1), 189–199 (2008).

### Acknowledgements:

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# P 13 - Mon

## SELF-ASSEMBLED NANOSTRUCTURES IN COPOLYMER BLENDS: SAXS, SANS AND TEM STUDY

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Phenomena associated with the phase behaviour and self-assembled nanostructures of three block copolymer systems have been studied by small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS) and transmission electron microscopy (TEM).

1) System A-*b*-B/A (*d*PS-*b*-PMMA/PS homopolymer) were studied as a function of molecular weight and concentration of the added homopolymer. The parameter  $r_M = M_H / M_C$  (molecular weight of homopolymer  $M_H$  to that of corresponding block copolymer chain  $M_C$ ) was selected to encompass all possible types of mutual homopolymer/block copolymer sizes. It has been shown that the parameters  $r_M$  and  $\chi^{3/2}N$  stipulate the slope of  $D$  vs  $w_p$  relation in the weak and the intermediate segregation regimes.

2) System (A-*b*-B)<sub>1</sub> / (A-*b*-B)<sub>2</sub> ( where A is perdeuterated polystyrene (*d*PS) and B is deuterated or hydrogenated poly(methyl methacrylate) (*d*PMMA or PMMA). The domain spacing  $D$  of the blends can be scaled with  $M_n$  by  $D \sim M_n^{2/3}$  as predicted by postulate introduced by Hashimoto at al. (originally suggested and proved for blends of lamellar PS-*block*-PI copolymers).

3) System A-*b*-B / A-*b*-C i.e. with one block in common ( $A = dPS$ ,  $B = PMMA$ ,  $C = PI$ ). One copolymer is in disordered microdomain state, while the other displays lamellar morphology at ordinary temperatures. Phenomena associated with the order-disorder transition (ODT), microdomain morphology and phase behaviour was investigated as a function of concentration of the added microphase-separated copolymer and temperature.

## P 14 - Mon

### HYDROPHILIC POLYMERS AS VERSATILE TOOL FOR PREPARATION OF SUPRAMOLECULAR SYSTEMS

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Proper function of bio-macromolecular systems is frequently critically dependent on formation of structurally well defined and self-organized supramolecular assemblies of macromolecules. Large molecules have many adhesion modes and the proper folding and 3D arrangement of macromolecules in the system would be often impossible without sophisticated systems (chaperons, etc.). However, in many cases much simpler tools can be used to get a unique structure.

We introduced a new concept of "**protein surface shielding agents**" (**PSSA**) which facilitates preparation of different supramolecular associates (trimers, hexamers, etc.) from identical macromolecules. **PSSAs** are molecules that bind temporarily to the specific areas on the surface of target proteins diminishing thus probability of formation of associates utilizing this part of surface. Series of different **PSSAs** offer an easy way to prepare different molecular clusters originating from different adhesion modes.

We studied the contact areas and the principle adhesion modes for several hundreds of experimentally confirmed polymer-protein interactions and compared them with the protein-protein interactions found in the crystalline phase [1]. This led to conclusion that polymers (MW~0.5-10 kDa) are suitable candidates for **PSSA**. The successive study led to design of a series of **protein surface shielding agents** of the type **E1-polymer1-linker-polymer2-E2**. Polymer segments are here POE oligomers

Experimental scan of activity of these water soluble polymers and copolymers led to more careful tests of sixteen polymers for their efficiency in protein crystallization. Six of them showed outstanding properties and were selected as precipitants for two new protein crystallization screens (POLYA, POLYB). The screens were tested in six laboratories on 30 different globular proteins.

Important applications of **PSSAs** are in protein structure determination because they facilitate experiments with identical protein in different environments (different hydration, space group, etc.). **PSSAs** can also prevent formation of disordered systems, can increase quality of crystals and thus contribute to higher accuracy of structure determination. The project is supported by GA AV IAA500500701.

[1] Hašek J., Zeitschrift für Kristallogr., 2006, 23, 613-618.

## P 15 - Mon

### NEW POLYPLEXES FORMED WITH CHOLESTEROL MODIFIED POLYCATIONS

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Polyplexes are polyelectrolyte complexes between DNA and polycations designed for gene delivery. In this study we investigated the properties of new polyplexes formed between cholesterol modified polycations and DNA as a potential non-viral gene transfer system with enhanced DNA uptake into cells by added biodegradable cholesterol groups. Three cationic polymers were tested (Fig. 1). Content of cholesterol was 4, 6 and 10 mole%. UV spectroscopy showing a shift of 260 nm absorbance maximum of DNA and fluorescence assay using ethidium bromide proved polyplexes formation. Titration by NaCl with a monitoring of DNA absorbance at  $\lambda=260$  nm revealed that complex stability increases with the increasing cholesterol content. Kinetics of turbidity of polyplexes solutions in the physiological solution shown that colloidal stability of polyplexes increases with increasing content of cholesterol side chains in polycations used to DNA condensation. Dynamic, static and electroforetic light scattering, small angle X-ray scattering and AFM were additionally used for characterization of polyplexes and also confirmed complex formation. Observed hydrodynamic radius of polyplexes was in the range 30-60 nm (Fig.2). and depends on composition ratio of polycation/DNA and hydrophobicity of used polycations (mol% of cholesterol groups). Particle properties of polyplexes depend, besides polycation chemical composition, also on the speed of polycation adding to DNA solutions.

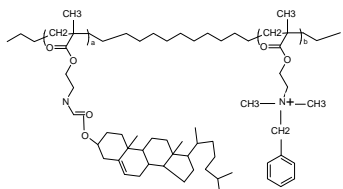


Fig. 1 Chemical structure of polymers.

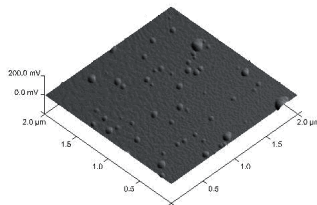


Fig.2 AFM images of polyplex P18 (1% Chol)+DNA

<sup>1</sup>Midoux, P.; Breuzard, G.; Gomez, J.P.; Pichon, Ch. *Current Gene Therapy*, **8**, 2008, 335-352(18)

## P 16 - Mon

### THE OXIDATION OF ANILINE WITH SILVER NITRATE IN THE SOLUTIONS OF ACETIC ACID TO POLYANILINE–SILVER COMPOSITES

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The reaction between two non-conducting chemicals, aniline and silver nitrate, yields two conducting components, polyaniline (PANI) and metallic silver. Such conducting polymer composites combine electrical properties of metals and materials properties of polymers [1]. Aniline was oxidized with silver nitrate in the solutions of acetic acid. The structure and properties of composites were characterized by Fourier-transform infrared (FTIR), Raman, and UV–visible spectroscopies, [thermogravimetric analysis](#), density, and conductivity measurement. True PANI–silver composites are produced only at moderate concentrations of acetic acid, 0.2–1 mol L<sup>-1</sup>, if sufficient time of several weeks is allocated for the reaction. This is confirmed by UV–visible, FTIR, and Raman spectroscopies [2,3]. The highest conductivities of composites were of the order of 10<sup>3</sup> S cm<sup>-1</sup>. The decisive role of the silver in the conductivity of composites is proved by the temperature dependences, which correspond to the metallic character of the samples. Polyaniline was present as nanotubes or nanobrushes composed of thin nanowires, as well as other morphological objects. Silver is produced mainly in clusters of nanoparticles having 30–50 nm size, nanowires or nanorods coated with PANI, and as the marble-like texture decorating some objects.

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## P 17- Mon

### SYNTHESIS OF GRADIENT POLYANILINE–POLYSTYRENE PARTICLES

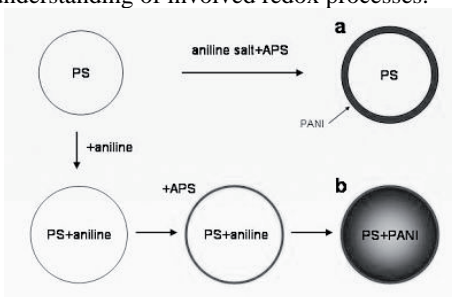
N.V. Blinova<sup>a</sup>, S. Reynaud<sup>b</sup>, M. Trchová<sup>a</sup>, J. Stejskal<sup>a</sup>

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New view on the modification of latex particles with conducting polymers is proposed. In contrast to the coating of latex particles with a polyaniline (PANI) overlayer resulting in a core–shell morphology, the interfacial type of reaction with separated reactants has been demonstrated. While in the former approach, anilinium salts soluble in aqueous phase are objects of oxidation, in the latter case these are neutral aniline molecules swelling latex particles. Liquid aniline is good solvent of PS, and it concentrates inside PS particles. The oxidant was then added to the aqueous phase surrounding latex particles (Figure). The monomer and oxidant molecules were separated by the PANI membrane, produced at the beginning of reaction at the surface of particles where the reactants met.<sup>1</sup> Aniline was polymerized inside the latex particles, gradually penetrating them as a result. The fact that the synthesized conducting polymer is able to transfer electrons from aniline molecules to the oxidant, and thus support the oxidation of aniline to PANI, is essential for the understanding of involved redox processes.



**Figure.** (a) The classical formation of a core–shell PANI-coated latex and (b) the proposed formation of composite polyaniline–latex particles.

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# P 18 - Mon

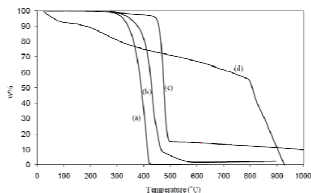
## SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE NANOPARTICLES AND THEIR NANOCOMPOSITES WITH POLYPROPYLENE

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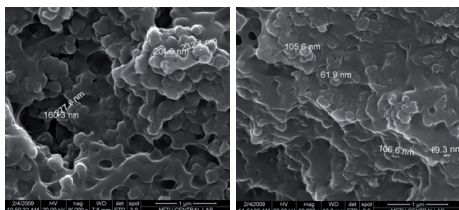
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<sup>b</sup>Department of Chemistry, Middle East Technical University, Turkey

Conducting polypyrrole (PPy) nanoparticles were synthesized via microemulsion polymerization system at low temperature. Nanocomposites were prepared by melt-mixing of polypyrrole with polypropylene (PP) and was processed with injection molding. The amount of PPy in nanocomposites varied in the range of 1-20% by weight. The effect of polypyrrole nanoparticles on mechanical, electrical properties and thermal stability of nanocomposites were investigated. The characterization of PPy nanoparticles was done by Fourier transform infrared spectrometer (FTIR) and scanning electron microscope (SEM). Tensile test revealed that increasing amount of PPy increased the strenght and the stiffness of the nanocomposite while limiting the elongation of PP. Thermal gravimetric analysis showed that incorporation of polypyrrole nanoparticles has improved the thermal stability of the nanocomposite (Fig.1). Four probe conductivity measurement exhibited that increasing amount of PPy nanoparticles increases the conductivity of nonconductive PP up to  $2,4 \cdot 10^{-4} \text{ Scm}^{-1}$ . In order to improve the dispersion of PPy in PP, identical procedures were employed using sodium dodecylsulphate as dispersant. SEM micrographs revealed that PP/PPy 1% and PP/PPy 5% nanocomposites prepared with dispersant exhibited better dispersion compared to ones that do not contain dispersant (Fig.2).



**Figure 1.** TGA plots of (a) virgin PP, (b) PP/PPy 10%, (c) PP/PPy 20% nanocomposites, (d) PPy



**Figure 2.** SEM micrographs of nanocomposites (a) PP/PPy 5%, (b) PP/PPy 5% with dispersant



## P 19 - Mon

### NANOPARTICLES AND THIN FILMS MADE FROM BLOCK COPOLYMERS AND THEIR DECORATION WITH POLYSACCHARIDES

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Polysaccharide-coated nanoparticles with controlled surface properties are very attractive candidates for biomedical applications since they are natural compounds exhibiting biocompatibility<sup>1,2</sup>.

This work is devoted to 1) find easy methods to prepare nanoparticles (micelles, vesicles,...) and thin films taking advantage from the self-assembly process in block copolymer systems; 2) their decoration by polysaccharides and 3) their characterisation with the state-of-the-art techniques such scattering and imaging. Among the systems we are investigating is the polystyrene-*b*-polyacrylic acid (PS-PAA) decorated with chitosane. In this specific case, the decoration is mainly driven by the electrostatic interactions between positively charged ( $\text{NH}_3^+$  groups) of the polysaccharide and the negatively charged surface of the nanoparticles ( $\text{COO}^-$  groups) or the nano-organized thin film with controlled phase.

The role of the electrostatic interactions is of great importance in this system and here we report some preliminary results on the  $\zeta$ -potential and the size of the nanoparticles with and without addition/adsorption of chitosan. For instance, dynamic light scattering and transmission electron microscopy measurements show after adsorbed chitosan layer, a narrow nanoparticles size distribution. Other experimental investigation are being pursued on the decoration at the nanoscale level on thin films.

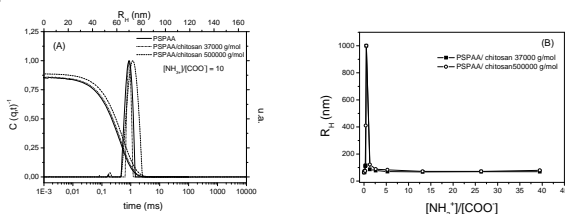


Figure 1. Dynamic Light Scattering measurements: correlation functions and size distribution (Left) and mean hydrodynamic radius of the nanoparticle (Right).

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## P 20 - Mon

### EXCITON DIFFUSION LENGTH IN FLUORENE - THIOPHENE BASED COPOLYMERS DETERMINED BY THE SURFACE PHOTOVOLTAGE METHOD

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The surface photovoltage method was used for the study of **FIPT** and **FPyT** copolymer layers (Fig.1) particularly for the determination of exciton diffusion lengths. The surface photovoltage (SPV) in a polymer layer is the result of dissociation of photogenerated free excitons in electric field of the space charge region (SCR), which forms spontaneously at the surface. Our conception of the SPV calculates both currents from the bulk and currents from the SCR where recombination is considered. Fitting theory to the experimental data allows estimation of the diffusion length and the thickness of the SCR regardless of the thickness of the layers. Much thicker SCR in **FIPT** than in **FPyT** was found. The evaluation indicates a high recombination rate in quite thick SCR of the **FIPT** layers, which agrees with high PL intensity in these films. For both materials it is shown that the main contribution to the photovoltage comes from the bulk region. For the copolymers under study the diffusion length was determined to be from 20 to 23 nm.

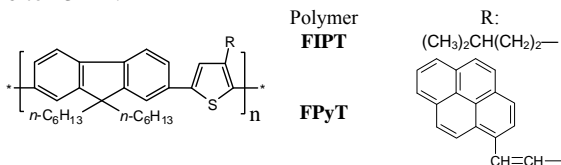


Fig.1

#### Acknowledgements:

We acknowledge the support of the Ministry of Education, Youth and Sports of the Czech Republic (grant No.1M06031 and MSM 0021620834) and the Grant Agency of the Czech Republic (grant No. 202/09/1206).

## P 21 - Mon

### SILICA-IONIC LIQUID HYBRID FOR THE PREPARATION OF POLYETHYLENE COMPOSITES

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Polyethylene is one of the most explored polymer matrixes for industrial applications, which is mainly due to its low density, good processability and low cost. However, the use of the neat matrix is restricted due to several drawbacks, including low strength and poor heat resistance [1]. The use of silica filler for the preparation of polyethylene–silica composites changed this profile and allows the formation of high performance materials [1,2]. Dispersion of the polar silica filler in the apolar polyethylene matrix is a challenge and the use of agents that reduce the interfacial repulsion is required [3]. In this perspective, surfactants and compatibilisers are an easy and cheap alternative to obtain these results. Ionic liquids (ILs) are organic salts with melting points below 100 C and are materials with differentiated properties, which turn them attractive for a broad range of scientific and industrial applications [4]. Lately, ILs showed exerting influence on the silica structure/properties when applied in the sol-gel system [5]. The IL present in the silica structure could act as a new type of coupling agent due to its surfactant like structure. In this work is reported for the first time the application of silica-IL hybrid (*in situ* imidazolium-IL modified sol-gel silica) as filler in the preparation of low density (LDPE) and high density (HDPE) polyethylene–silica composites. The silica-IL hybrid was characterized by SEM and AFM, and the polymeric composites were characterized by TEM, TGA and DMA. This innovative technology resulted in the formation of polyethylene–silica composites with improved thermal stability and mechanical properties. Furthermore, the IL improved the silica dispersion, which suggests that the IL increases the interaction between the filler and the matrix.

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## P 22 - Mon

### THE INFLUENCE OF IONIC LIQUIDS ON THE *IN SITU* FORMATION OF EPOXY – SILICA NANOCOMPOSITES

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The *in situ* formation of epoxy – silica nanocomposites offers several benefits. One of the most important consists in the fine dispersion of the inorganic phase in the organic matrix, as a consequence of the molecular mixing of reactants [1]. Furthermore, it is possible to control the structure and morphology by reaction conditions, allowing the preparation of tailored products. Another form of affecting the filler's structure is the use of *templates*, which could force the silica orientation and organization. Ionic liquids (ILs) are organic salts with melting points under 100 C, presenting differentiated properties that have attracted considerable interest for scientific and industrial applications. Lately, ILs showed exerting influence on the silica structure/properties when applied in the sol-gel system [2]. In addition to directing silica's morphology, the use of IL as an additive could produce an *in situ* epoxy-silica nanocomposite that "inherit" these advanced IL characteristics, affecting thermal and mechanical properties. The epoxy-silica nanocomposite system produced in this research was obtained by simultaneous formation of nanosilica filler and the organic matrix. The first synthetic step consisted in the sol-gel reaction in the presence of ILs. In the second step, the hydrolyzed sol was introduced in the epoxy system; diglycidyl ether of Bisphenol A – diamine. The structural and morphologic properties of the products were characterized by SAXS and TEM analysis. The influence of IL on the silica formation, the thermo-oxidative resistance and the mechanical properties of the nanocomposites were investigated by NMR, TGA and DMA, respectively. The formed nanocomposites exhibited enhanced thermal and mechanical properties. The ILs showed an effect on improvement of filler dispersion within the matrix and on the ordering of the system.

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## P 23 - Mon

### NOVEL SOLUBLE FLUORENE – THIENOTHIADIAZOLE AND FLUORENE – CARBAZOLE COPOLYMERS FOR OPTOELECTRONICS

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Novel soluble low-bandgap fluorene – thienothiadiazole based copolymers, **CHTF** and **CDTF**, and luminescent fluorene – carbazole copolymers, **CFCzE** and **CFCzA**, were synthesized (Figure 1) and their optical, photophysical, electrochemical and photoelectrical properties studied. Copolymers **CHTF** and **CDTF** in solutions exhibit solvatochromism and thermochromism strongly supported by the alkyl chains on thiophene rings. In thin films strong intermolecular interactions play an important role. The long-wavelength absorption maxima at 750 – 785 nm are significantly red-shifted compared to those in solution. The copolymers **CHTF** and **CDTF** possess low bandgap, high electron affinity and exhibit reversible electrochromic behavior. Therefore they are of interest for electrochromic and photovoltaic applications. Spectroelectrochemical study was performed and optical switching was demonstrated. Photovoltaic devices with bulk heterojunction made of blends of **CHTF** or **CDTF** and fullerene derivative PCBM were prepared. The power conversion efficiency was 2-3 %. On the other hand the fluorene-carbazole copolymers, which exhibit blue photoluminescence (PL) with high quantum efficiency, are candidates for light-emitting applications. Light-emitting devices with intensive broad blue-white emission were fabricated.

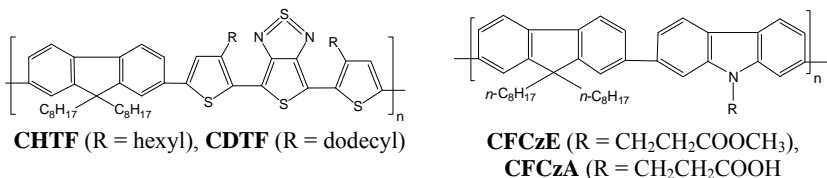


Figure 1.

Acknowledgement.

We would like to acknowledge the support of the Ministry of Education, Youth and Sports of the Czech Republic (grant No.1M06031).

## P 24 - Mon

### LAYERS OF INORGANIC-ORGANIC MATERIALS PREPARED BY SOL-GEL METHOD

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Inorganic-organic hybrid polymers of the type Ormocer (ORganically MODified CERamics) belong to new hi-tech material. Inorganic-organic hybrid layers based on 3-(trimethoxysilyl) propylmethacrylate (TMSPM) were prepared by modified sol-gel method. Layers were tested on various substrates (glass, corundum ceramics, aluminium, polyester, polyamide, polypropylene). Besides the pure hybrid layers, also layers with encapsulated textile dye-salteries or nanoparticles of titanium dioxide were investigated. Hybrid polymer layers had thickness of 50-100 nm.

The layers of polymerized monomer had excellent chemical resistance towards concentrated inorganic acids ( $H_2SO_4$ ,  $HNO_3$ , HF), alkaline hydroxide (30 % NaOH) and organic solvents e.g. hot toluene. The properties of layers differed according to the way of their preparation. Added components (textile dye-salteries or titanium dioxide nanoparticles) were strong fixed in the hybrid layer.

**Key words:** sol-gel method, hybrid coating, Ormocer, nanocomposite

## P 25 - Mon

### **STRUCTURAL CHARACTERIZATION OF EDIBLE ZEIN FILM BY FT-RAMAN SPECTROSCOPY**

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Zein film draws much interests being an edible film/coating for food packagings and other applications because of its biodegradable property and hydrophobic characteristics. The distinct properties of zein-based biodegradable films, including mechanical properties, water absorption, and barrier properties, depend on their three-dimensional network structure and on the interaction between proteins, plasticizers, and other functional agents. We reported here the preparation of zein film directly from zein protein and then used near-infrared Fourier transform Raman (FT-Raman) spectroscopy to characterize its molecular structure. Based on the vibrational modes of amide I at  $1655\text{ cm}^{-1}$  and amide III at  $1274\text{ cm}^{-1}$ , the secondary structure of zein protein was mainly in  $\alpha$ -helix and remained unaltered during film formation. Raman results revealed that hydrophobic interaction played an important role in the formation of zein film and disulfide bonding might be responsible to the structural stability of zein protein during film formation. Both polar agent and UV radiation would cause film crisper resulting in lowering film quality. This might result from hydrophilic interference and tyrosine oxidation, irrespectively, in the film's microstructure as supported by Raman analysis on the state of phenolic OH group.

## P 26 - Mon

### ON THE EFFECT OF RANDOMNESS OF PARTICLE SPACING ON THE VISCOELASTICITY OF POLYMER NANOCOMPOSITES

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Reinforcing mechanisms in amorphous polymers filled with submicron size fillers with very high specific surface area consists of two principal contributions: mechanical and molecular (1, 2). Above the glass transition of polymer matrix, the second contribution becomes the dominating mechanism. Droste and DiBenedetto (1) presented correct interpretation of data from mechanical measurements in late 60's without any results from computer simulations, which are available now. Recently, Sternstein et al. (3) proposed model of molecular mechanisms leading to increase of elastic modulus with nano-filler content above  $T_g$  of matrix substantially greater than predicted considering volume replacement only. In this contribution, a number of remarks to the theoretical concept published by Sternstein et al. (3) is presented based on recent results from simple stochastic model of non-uniform arrangement of particles in space. It was shown that irregular particle spacing in the matrix is an essential aspect of polymer nanocomposite reinforcement above  $T_g$  leading to strong chain confinement due to interactions with impenetrable filler surface (Figure 1).

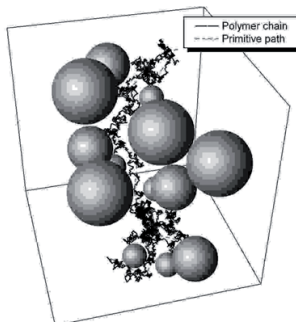


Figure 1: Illustration of the confinement problem.

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## P 27 - Mon

### **EFFECT OF SEVERAL PARAMETERS ON DIMENSIONAL AND RELEASE PROPERTIES OF ALGINATE MICROPARTICLES**

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Alginate microparticles are currently employed in a wide range of applications, including enzyme immobilization, cell encapsulation and drug delivery.

Alginate, a naturally occurring biopolymer extracted from brown algae, can be ionically cross-linked by the addition of divalent cations in aqueous solution. It has several properties that enable it to be successfully used as a matrix for the entrapment and/or delivery of biological agents. In particular proteins can be loaded and released by alginate matrices without loss of their biological activity because of the relatively mild gelation process of alginate.

In the present work alginate particles were produced by a water-in-oil emulsification process and calcium chloride ( $\text{CaCl}_2$ ) was used as cross-linking agent. The effect of different  $\text{CaCl}_2$  amounts and the mechanism of solvent elimination from the emulsion droplets on the particle morphology, dimension, encapsulation and release behaviour were investigated.

The morphological characteristics of the produced particles were analysed mainly by scanning electron microscopy (SEM). SEM images were used to perform a dimensional analysis. A model protein, insulin, was encapsulated into the particles and in vitro tests were performed to evaluate its release.

It was observed that the amount of  $\text{CaCl}_2$  used for alginate cross-linking slightly affects particle dimension only when the number of  $\text{Ca}^{2+}$  ions is lower than cross-linking sites of alginate. In this case slightly bigger particles are obtained because of a lower shrinkage of the polymer.

On the contrary the release kinetics of insulin was affected by the amount of  $\text{CaCl}_2$ . It was observed a slower release kinetics for a higher cross-linking degree even if the mechanism of release seems not to be controlled by a simple diffusion, and swelling phenomena have to be taken into consideration.

With regard to the study related to the mechanism of solvent elimination, performed by optical microscopic observation, it was concluded that the final dimension of the particles is not determined by cross-linking but instead it depends mainly on the complete solvent evaporation that goes on after the end of the cross-linking phase.

## One single composite for chemical sensor or heating purposes

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The major target of intrinsic conducting polymer (ICP) development is to combine the electrical properties of these materials with the mechanical and processability properties of commodity bulk polymers. Among ICPs, polyaniline (PAni) received a great deal of attention because of its easy preparation with low costs and its stability under environmental atmosphere. Moreover, the electrical conductivity of PAni can be closely controlled over a wide range coming from  $10^{-4}$  to  $10$  S.cm<sup>-1</sup> which makes PAni a good candidate for many applications<sup>1-4</sup> as antistatic films, electromagnetic shielding layers, sensors, technical packaging and anticorrosion.

The IPREM-EPCP group focused on the optimization of a simple way of synthesis to yield to a conducting composite in one-step<sup>5,6</sup>. The final aqueous dispersion contains composite particles made of polymer matrix and polyaniline and is used without post formulation. Conducting films are obtained by spraying or automatic film applicator methods. The conductivity and the chemical composition of the final composite may be in line with the target application.

The same conducting composite was then successfully used as chemical sensor and heating surface. The whole process, *i.e.* from the synthesis to the film forming, remain as simple as possible and are carried out in soft experimental conditions, that is, without external acid or organic solvent.

After a brief presentation of the synthesis and the characterization of the conducting films, the performances of chemical sensors and heating surface will be discussed. The study of chemical sensor demonstrated the feasibility of whole polymer sensors to detect ammonia<sup>7,8</sup>. Moreover, all performances of this new chemical sensor are in line with the market needs in terms of response time, sensitivity, reproducibility. At last, these sensors introduce a breakthrough technology since their response is reversible with no need of servicing or calibration between two exposures (Figure 1). This feature is very interesting in terms of time-life and cost.

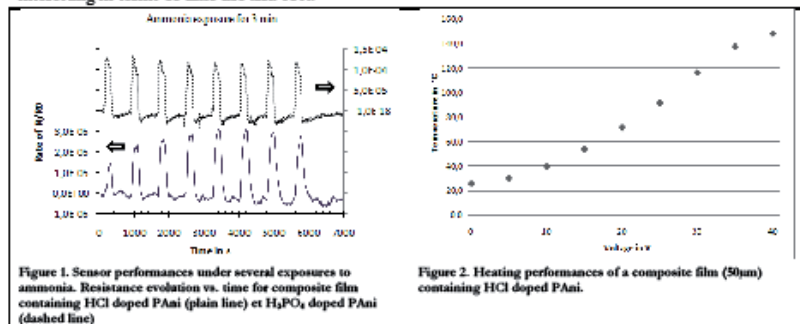
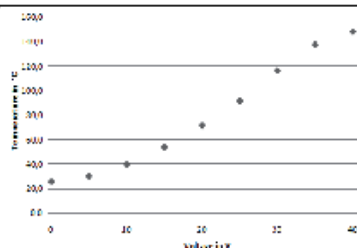


Figure 2. Heating performances of a composite film (50µm) containing HCl doped PAni.



The same composite films have been successfully tested as heating surface. The temperature of the films is measured via an Infra-Red camcorder and the results are reported Figure 2. Its heating performances and its processability (soft final material, easy to cut and pattern) allow considering its development as heating devices suitable for low energy building (tunable size, thin film, easy to handle).

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## P 29 - Mon

### **MORPHOLOGY OF POLYANILINE NANOPARTICLES SYNTHESIZED BY USING AN IONIC LIQUID AS A SOFT TEMPLATE**

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PANI nanostructures are becoming more and more interesting since they combine properties of organic conductors with properties of materials with large surface area. They are very promising material for applications in various fields. It is possible to prepare PANI nanoparticles by using ionic liquids as solvents or additives. The type of ionic liquid and experimental conditions have an essential effect on morphology and properties of the formed nanoparticles.

We prepared nanostructured PANI by chemical oxidation of aniline using ammonium persulfate as an oxidant in acidic water solution of the 1-butyl-3-methylimidazolium chloride. In this contribution we will present the effect of the ionic liquid, which acts as the soft template, on the properties and morphology of the formed PANI. We will also present how experimental conditions i.e. stirring and concentration of starting reaction mixture affect the morphology and properties of the PANI nanoparticles. Higher concentration of starting reaction mixture leads to bigger particles that are highly agglomerated. Stirring on the other hand does not have a great effect on the morphology. PANI nanoparticles were characterized using scanning electronic microscopy (SEM), spectroscopic methods (NMR, IR, UV-VIS), size exclusion chromatography (SEC) and impedance spectroscopy.

## P 30 - Mon

### PHYSICOCHEMICAL CHARACTERISATION OF POLYMERIC NANOPARTICLES STABILISED BY SURFACTANTS

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We have investigated self-organisation of polymers with surfactants resulting in formation of stable and uniform nanoparticles.

We have studied polymeric nanoparticles prepared by dispersion of poly(methyl methacrylate) and of polystyrene dispersed in water. The dispersion was prepared by a fast mixing a solution of the polymers with a solution of a surfactant in pure water. We observed the formation of well defined nanoparticles with hydrodynamic radii from 50 to 200 nm measured by light scattering methods. The particle formation is qualitatively explained by stabilisation of monodisperse nuclei of the polymers by a selected surfactant at the early stage of the phase separation of the polymers. Adsorbed surfactant hydrophilises the nanoparticle surface. If the amount of the adsorbed surfactant reaches the critical surface concentration, the growth of nanoparticles is stopped. Therefore, a structure of the particles is supposed to be similar to block copolymer micelles.

We have investigated solutions of the above mentioned polymers with several ionic and non-ionic surfactants. The study shows how nanoparticle properties are changed by the chemical composition of surfactants, molecular weight of polymers, concentrations of both components and finally, by variations in method of nanoparticles preparation. Static light scattering (SLS) and dynamic light scattering (DLS) provide the weight-average molecular weight  $M_w$ , hydrodynamic radius, radius of gyration and non-uniformity index for selected types of nanoparticles. In some cases, the light scattering results are compared with those obtained by small-angle neutron scattering (SANS) and cryo-TEM and AFM techniques.

We acknowledge support by the Grant Agency of The Czech Republic (grant SON/06/E005) within the EUROCORES Programme SONS of the European Science Foundation which is also supported by the European Commission, Sixth Framework Programme.

## P 31 - Mon

### SELF-ASSEMBLED ALTERNATING MULTILAYERS OF CONJUGATED POLYELECTROLYTES AND GOLD NANOPARTICLES

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Polymer nanocomposites containing noble-metal nanoparticles are promising materials for optoelectronic applications due to the local enhancement quenching of various photoinduced processes (Raman scattering, fluorescence, photoisomerisation). We present new nanostructured materials containing a three-dimensional metal nanoparticle assembly in combination with  $\pi$ -conjugated polymers.

Thin films consisting of  $\pi$ -conjugated polyelectrolytes, poly[3-(carboxymethyl)thiophene-2,5-diyl], P3ETCOOH and poly{3-[6-(1-methylimidazolium-3-ylbromide)hexyl]thiophene-2,5diyl}, P3HTIm, were prepared by layer-by-layer deposition from aqueous solutions. During this process, a solid substrate (quartz, mica, ITO) was consecutively immersed in aqueous solutions of the cationic P3HTIm and the anionic P3HTCOOH. The alternating layers are progressively deposited due to the electrostatic interactions of imidazolium and carboxyl groups as it was evidenced by optical absorption measurements.

The self-assembly process was further modified by adsorption of gold nanoparticles from a citrate gold nanosol. The layers of Au nanoparticles (diameter cca. 15 nm) deposited in between P3HTIm and P3ETCOOH layer bring about an additional extinction ascribed to a gold surface plasmon resonance. The position of the plasmon optical absorption maximum was shifted to longer wavelengths with the increasing number of deposited layers which can be explained by increasing dipolar interaction of surface plasmons within nanoparticles assembly.

Electrical properties of the thin films were tested using sandwich structures where the active materials were deposited between ITO and gold electrode. The nanostructured polymer composite was characterized by electrical conductivity in the order of  $10^{-9} \text{ Scm}^{-1}$  and corresponding sample with Au nanoparticles by electrical conductivity in the order of  $10^{-6} \text{ Scm}^{-1}$ .

## P 32 - Mon

### **HIGH-DENSITY POLY(ETHYLENE OXIDE) SURFACE COATINGS: THE EFFECT OF GRAFTING CONDITIONS ON THE STRUCTURE OF GRAFTED POLY(ETHYLENE OXIDE) LAYER**

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Poly(ethylene oxide)-based surface coatings have proven successful in suppression of nonspecific interactions of surfaces with proteins and cells that is a prerequisite for many biomedical devices, including drug delivery systems, tissue engineering scaffolds or label-free optical biosensors. Poly(ethylene oxide) coatings show the highest performance when they are in a state of polymer brush, which is, however, difficult to achieve by common solution “grafting to” methods. Recently, layers of poly(ethylene oxide) end-grafted to the supporting surface from melt through an anchoring layer of poly(glycidyl methacrylate) have been shown to have high chain density with significant overlap of adjacent polymer chains and, therefore, justifiably considered to be polymer brushes. This report shows, that the structure of PEO layer deviates from a simple polymer brush monolayer under certain grafting conditions, namely when the anchoring layer above certain thickness was used. The layer properties resulting from the grafting conditions leading to more complex layer architecture have been investigated by ellipsometry. Possible implications of PEO layer structure for the coating performance in above applications are discussed. The authors acknowledge the financial support from Academy of Sciences of the Czech Republic (grant No. 1QS500115064).

## P 33 - Mon

### “CLICK & SEED” APPROACH TO THE BIOMIMETIC MODIFICATION OF POLYMERS

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Functional surface modification of biomaterials for the cell adhesion is important not only for preparation of biodegradable scaffolds in tissue engineering, but also for model in vitro cell culture studies. To study the cell behavior in response to surface chemical modification, the surfaces with suppressed adsorption of extracellular matrix proteins from the culture media are needed. A method of surface modification that could be simply applied to commercially available cell cultivation dishes was studied.

Cell culture dishes modification protocol consisted of three steps: 1) modification of the polymer surface with polydopamine<sup>1</sup>, 2) grafting the PEO layer on the polydopamine surface and 3) “click-binding”<sup>2</sup> of the azidopeptide motif on the surface.

Polydopamine interfacial layer was formed using a reaction protocol described previously<sup>1</sup>; the grafting of PEO to polydopamine was performed by several methods (evaporation, melting under various temperature conditions) and compared. Cell adherence tests with modified surfaces were performed using mouse embryonic fibroblasts and NTERA-2 cell line cultivated in standard MEF medium.

The modification efficiency was significantly improved compared to previously published system<sup>1</sup> upon the this optimization. PEO-grafted surfaces with the cell adhesion reduced to about 1 % of the values for standard cultivation plastics were obtained. The cell proliferation activity was significantly decreased as well. The presence of propargyl group on the non-adhesive surface was shown to allow for further modification by “click addition” of azide group containing peptides.

THE WORK WAS SUPPORTED BY ACADEMY OF SCIENCES CR (GRANT NO.: KJB400500904).

References:

1. H. Lee et al., *Science*, 2007, 318(5849), pp. 426-430.
2. D.D. Diaz et al., *Journal of Polymer Science Part a-Polymer Chemistry*, 2004, 42(17), pp. 4392-4403.

## P 34 - Mon

### SYNTHESIS OF CONDUCTIVE POLYMERIC COMPOSITES OF SUB-MICROMETER SIZED PARTICLES AND ELECTRICAL CHARACTERIZATION OF THIN FILMS PREPARED THEREFROM

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During the last decade an interest in conducting polymers strongly increased on both scientific and application level. However, the electrically conductive unsubstituted polymers are not well soluble, which prohibits them from many direct applications. This could be solved by preparation of the polymers in form of particle dispersions.

Preparations of two types of core-shell and one type of nanogel composites are described. The particles in the former case consist of the insulating core of polystyrene-copolymers that is covered with conductive PPy (cf. Fig. 1) or PEDOT shell. Nanogels are composed of PEDOT grains embedded into crosslinked electrically insulating polymer bodies consisting of another polystyrene-copolymer. The electrical conductivities, its dependences on temperature, frequency and humidity were measured. The results obtained are correlated with composite morphology, proportion of its components and parameters of synthesis.

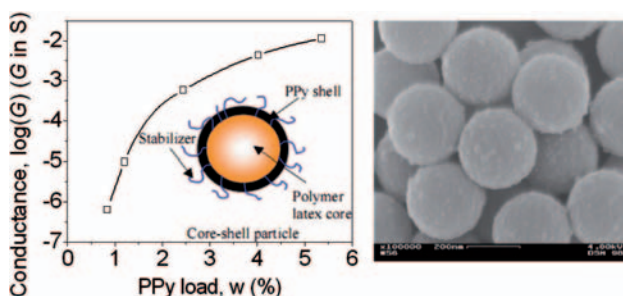


Fig. 1: Core-shell particle composite based on PPy. Conductance of thin film versus the PPy proportion in the composite – left; structure drawing of single particle – the inset; SEM micrograph of the thin film – right.



## P 35 - Mon

### SOLUBLE PHTHALOCYANINES AS NITROGEN DIOXIDE SENSORS

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There is a growing interest in fast and reliable gas sensors. NO<sub>2</sub> detection is important for environmental monitoring and life safety. Phthalocyanines (Pcs) are known to be sensitive to NO<sub>2</sub>, but their electrical responses are not stable and very often not fully reversible. Additionally, the deposition of thin films of non-substituted Pcs is complicated and requires a high vacuum technique. In this paper we present the results of the studies of the NO<sub>2</sub> influence on electrical, photoelectrical and optical properties of soluble 3-diethylamino-1-propylsulfonamide zinc and metal-free phthalocyanines (ZnPcSu and H<sub>2</sub>PcSu, resp.).

According to optical (absorption spectrum) detection different mechanisms were found for the NO<sub>2</sub> sensitivity of both phthalocyanines under study. It is shown, that above mentioned Pcs are reversibly sensitive to NO<sub>2</sub> even at room temperature. A new charge transfer band at 500 nm appears in the UV-VIS absorption spectrum of ZnPcSu, while the spectrum of H<sub>2</sub>PcSu remains unchanged after NO<sub>2</sub> exposure. Electrical conductivity of ZnPcSu film increases up to two orders of magnitude in NO<sub>2</sub> atmosphere while the conductivity of H<sub>2</sub>PcSu decreases if exposed by the same concentration of analyte gas.

Using quantum chemical calculations it was found the formation of charge transfer ZnPcSu-NO<sub>2</sub> complex with the molecule of the gas coordinated to the central Zn atom. Electrical conductivity of the ionized complex is higher and strongly influences the sensor response. H<sub>2</sub>PcSu does not form the complex; the decrease of the conductivity can be explained by the intercalation of NO<sub>2</sub> species between Pc units in the molecular Pc stack.

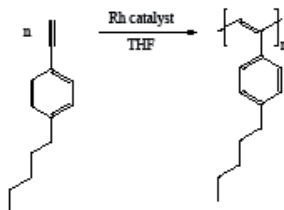
This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (grant KAN400720701).

## SEC/MALS AND $^1\text{H}$ NMR STUDY OF POLY[(4-n-PENTYLPHENYL) ACETYLENE]: SOLUTION PROPERTIES AND MOLECULAR-WEIGHT AND CONFIGURATIONAL STABILITY

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High molecular weight ( $M_w = 2 \cdot 10^6$ ), high-cis poly[(4-n-pentylphenyl)acetylene] (PPePhA) was prepared by polymerization of (4-n-pentylphenyl)acetylene with  $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{Ph}_2\text{C}=\text{C}(\text{Ph})\text{Li}/\text{PPh}_3$  catalyst.



1) THF solution of PPePhA was studied in detail by Size Exclusion Chromatography coupled with concentration and Multi Angle Light Scattering detectors (SEC/MALS). This approach allowed: (i) comparison of absolute and on PS calibration based apparent MW characteristics and subsequent determination of constants of Kuhn–Mark equation, (ii) determination of  $R_g$  vs.  $M$  relationship and subsequent determination of unperturbed dimensions. Results revealed the random-coil behavior of PPePhA in THF (in despite of the main chain conjugation).

2) Using SEC/MALS and  $^1\text{H}$  NMR techniques the long term molecular-weight and configurational stability of PPePhA dissolved in THF was studied in the temperature range from  $-30$  to  $50^\circ\text{C}$ . Results obtained showed expected oxidative degradation that was in the whole temperature interval accompanied by cis-trans isomerisation. These processes, however, exhibited different rate vs temperature dependences.

### Acknowledgement:

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# P 37 - Mon

## EFFECT OF ADDITIVES ON STABILITY OF POLYMER GLOBULES

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The effect of phase separation in polymer solution results in the formation of polymer globules. These globules can be described as insoluble solid-like particles evenly distributed in the solvent. Difference in the separation temperature for hydrophilic and hydrophobic parts of the polymer chain can be the reason of the presence of solvent molecules inside the globules. Mobility of these “caught” (or “bound”) solvent molecules is limited inside the globule pores. Another part of the solvent molecules is unrestricted in mobility and “free” from interaction with polymer globules. The time of stabilization and reorganization processes inside the polymer globules-water system strongly depends on flexibility of polymer chains as well as on the intensity of polymer-polymer and polymer-solvent interaction inside the globular structure.

Two different additional solvents were chosen. One of them is tert-butyl methyl ether (MTBE) where the interaction with polymer is negligible (in case of PVME) or very weak (in case of PIPMAm and PIPAm). It was supposed that mobility of MTBE corresponds to the behaviour of free water components. Hydroxylamine was chosen as a second additive solvent, characterized by the strong interaction with the both components in mixture (water and polymer).

The presence of these solvents can lead to changes in character of interaction between polymers and solvent and that interactions between both solvents are also important. For both additional solvents it was found that already 5 mol-% of the additives is enough to completely change the behaviour of the polymer. In the case of MTBE as the additive solvent the precipitation effect was observed in 15 minutes and no chemical exchange effects were detected.

### **Acknowledgment:**

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## P 38 - Mon

### ELECTRIC AND DIELECTRIC PROPERTIES OF POLYANILINE/MONTMORILLONITE COMPOSITES

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Electric properties of polyaniline (PANI)/montmorillonite (MMT) composites as a system composed of a conducting organic polymer, PANI, dispersed in insulating matrix of MMT have been studied in effort to find an influence of concentration of PANI, the polymerization process, and the origin of MMT on electric conductivity. Two ways of PANI preparation on three samples of MMT were tested: a direct oxidation of aniline hydrochloride with ammonium peroxydisulfate [1] in the presence of MMT (set A), and the similar process, when aniline was intercalated into MMT at first (set B).

Measurements of electric properties were done on compressed pellets. DC resistivity was measured by four-point method in van der Pauw configuration at temperature range 77–318 K; gold electrodes were deposited on more resistive samples and measured by an electrometer. Dielectric spectroscopy was done using a Novocontrol dielectric  $\alpha$ -analyzer at temperatures 113–303 K. At room temperature, a strong growth of DC conductivity in the dependence on PANI concentration near 15 % was observed. It is believed in these composites percolation mechanism occurred. No significant qualitative differences between sets A and B in DC conductivity and different types of MMT were found. Temperature dependences in the range of 85–225 K of DC conductivity are well described by quasi-1D variable-range hopping transport mechanism in agreement with [2]. AC measurements show conductivity contribution at low frequencies and relaxation contribution at high frequencies. Measured conductivity confirms hopping at low temperatures. For high concentration of PANI, a Debye-like relaxation behavior has been observed. A broad distribution of relaxation times with Arrhenius-like temperature dependence has been found for low concentrations of PANI.

[1] Stejskal J. Gilbert R.G., Pure Appl. Chem. 74, 857 (2002).

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## P 39 - Mon

### **HARDNESS AND TENSILE PROPERTIES OF EPOXY-BASED NANO PARTICLE-REINFORCED COMPOSITES**

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Nanocomposites using thermoplastic polymers are well known for improving the mechanical, electrical, thermal and insulating properties. However, nanocomposites using thermosetting polymers have not been studied so extensively, particularly using TiO<sub>2</sub> particles as reinforcing agent. The objective of this research work, was to fabricate epoxy-based nanocomposites containing various amounts of TiO<sub>2</sub> particles. Mixing procedures were done by sonication in order to disperse the particles in the resin matrix uniformly. Hardness and tensile tests were performed on the composite samples with the aim to improve the above-mentioned mechanical properties and also see the effect of reinforcement loading on these properties. The experimental data indicated that, hardness of the composites increased nonlinearly with increasing the concentration of nano TiO<sub>2</sub> particles and also with respect to the neat resin system. Hardness data also indicated that the time-dependent hardness of the composites was not affected by the filler content. It was indicated from the tensile data that both the tensile strength and modulus increased in presence of TiO<sub>2</sub> nano particles and also with incremental particle loading.

## P 40 - Mon

### **THERMAL STABILITY AND DYNAMIC MECHANICAL PROPERTIES OF EPOXY/ NANO AND MICRO TiO<sub>2</sub> COMPOSITES: EFFECT OF MIXING METHODS**

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This research work focuses on the performance optimization of composites containing both micro and nano size TiO<sub>2</sub> particles separately in various concentrations and to understand the role of each on the thermal stability and moduli of the composites. Thermal stability of the particle-reinforced composites increased on increasing the concentration of TiO<sub>2</sub> both in nano- and micro- filled cases, except for the 2.5wt% nano-filled composite. Storage modulus (E') increased on adding micro-TiO<sub>2</sub> to the epoxy hardener resin system from 1 - 2.5 - 5 wt% respectively and decreased dramatically on further increasing the micro-TiO<sub>2</sub> content to 7.5 and 10 wt% respectively. Nano-TiO<sub>2</sub> particle-reinforced composites showed an increasing trend of storage modulus for 2.5 – 5 - 7.5 wt% TiO<sub>2</sub> filled composites with respect to the neat resin system. Presence of both micron and nano-TiO<sub>2</sub> particles increased the T<sub>g</sub> of the composites. Also the effect of sonication on the modulus and T<sub>g</sub> has been discussed.

## P 41 - Mon

### PHOTOSTABILIZATION AND PHOTODEGRADATION OF POLY[METHYL(PHENYL)SILYLENE]

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Polysilanes are not very stable under UV exposure. According to IR studies oxidative changes in model polymer poly[methyl(phenyl)silylene] (PMPSi) exposed by UV light led to the increase in absorption in the siloxane, carbonyl, and hydroxyl regions, the decrease in absorption in the Si–Si region, and the changes in the aromatic C–H bond region. The quantum efficiency of bond scission was determined as 0.016 for solid films and 0.51 for tetrahydrofuran solution. The photooxidation can be retarded by triazine- and oxalanilide-based absorbers [2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)phenol (I) and *N*-(4-*tert*-butyl-2-ethoxyphenyl)-*N'*-(2-ethylphenyl)oxalanilide] (II) protecting the polymer by the excited state intramolecular proton-transfer mechanism. The best result was obtained with the mixture of the material (I) with bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate.

For some applications, e.g., lithography, an enhanced degradation under UV light or electron beam exposure is necessary. Polysilanes seem to be good candidates for nanolithography in the area of silicon technologies. Efficiency of the degradation process can be increased by acceptor-like side groups or additives. The best result was obtained using benzoquinone. However, a back electron transfer from phenyl (PMPSi) or the additive to the main chain results in the decrease of the decomposition efficiency. This difficulty was overcome using an additive with unstable anion radical. After the electron transfer from the PMPSi chain, the anion radical of the additive decomposes and back electron transfer is impossible. The best efficiency of this process was obtained using benzoylperoxide as the additive.

The model was supported by quantum chemical calculations. The additive molecules were assumed to act as degradation catalysts. It was shown that emerged anions subsequently attack, among others, positively charged Si-chain causing its scission.

The work was supported by the European Commission through the Human Potential Programme (Marie-Curie RTN BIMORE, Grant No. MRTN-CT-2006-035859) and by the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. IAA100100622).

# P 42 - Mon

## **SURFACE PROPERTIES OF POLYMERS**

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Surface properties of most materials, including polymers, represent a fundamental factor in terms of their applications. Therefore, considerable attention is paid to research in the field of interfacial phenomena<sup>1</sup>, whose findings can be useful for the application of polymers in such areas as bioengineering.

In this study, polarity of hydrophilic methacrylate copolymers based on 2-hydroxyethyl methacrylate (HEMA) with glycidyl methacrylate (GMA) and glycerol monomethacrylate (GMMA) with 2-ethoxyethyl methacrylate (EOEMA) and some commercial polymers was evaluated by measuring the surface tension, contact angle and swelling capacity. The surface tension of poly(HEMA-co-GMA) copolymers, as well as swelling degree decreases with the increasing GMA content. The poly(EOEMA-co-GMMA) surface tension decreases with the increasing content of GMMA, but the swelling degree increases. Surface tension of commercial polymers decreases from 47 mN/m for PET to 23 mN/m for PS. The so-called hydrophilic polymers based on HEMA and GMA or EOEMA and GMMA exhibit surface tension 34 mN/n and lower, which are similar to those for PET and PS. The low values of surface tension and high values of contact angles suggest that the interaction between these polymers and the aqueous media are particularly determined by dispersion forces, which prevail over the polar interaction.

### **Acknowledgements**

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[1] P. Chen, Ed., Molecular Interfacial phenomena of polymers and biopolymers, University of Waterloo, Canada, ISBN 1 85573 928 3 ISBN-13: 978 1 85573 928 4 July 2005



## P 43 - Mon

### THE INFLUENCE OF ORGANICALLY MODIFIED LAYERED SILICATES ON PROPERTIES OF ORGANIC-INORGANIC NANOCOMPOSITE COATINGS

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Two commercial layered silicates (LS), Montmorillonite (Cloisite® Na, Southern Clay Products) and Bentonite for water systems (Fluka) were modified by organic compounds containing hydroxyl groups (polyethylene glycol, Polysorbate, etc.). These organically modified LS (dispersed in water) were incorporated into organic-inorganic (O-I) matrix. The concentration of modified LS in the product varied from 0.3 to 0.65 wt. %.

Nanocomposites were prepared in the form of coatings and free-standing films: O-I hybrids were prepared on the basis of two consecutive and independent processes: sol-gel process (*in situ* build-up of inorganic structures with epoxide-functions from functionalized organosilicone precursors) followed by polyaddition reaction (epoxy network formation with amines). The dispersions of LS were added just before beginning of epoxy network formation (i.e., in the presence *in situ* formed of inorganic building units containing glycidyl groups). These transparent and colorless coatings or free-standing films featured by high degree of self-assembly of O-I matrix. Modified LS are partly intercalated, partly exfoliated in the O-I matrix (as detected by WAXS experiments).

It was found that already very small amount of organically modified LS markedly influence tensile properties. If toughness (i.e., the energy per volume necessary to break the sample) is considered as a criterion of quality and hence usability of O-I products, better results were achieved with bentonite-containing samples compared to montmorillonite analogues. Optical microscopy confirmed good and regular self-organization of LS on coating surfaces; the shape and size of formations depends not only on the type of LS and its modification but it is also influenced by the constitution of the O-I matrix itself.

#### Acknowledgements

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## P 44 - Mon

### THE CHEMICAL MODIFICATION OF POLY(A-AMINO ACIDS)S FIBRES FOR TISSUE ENGINEERING APPLICATIONS

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Three-dimensional constructs based on fibres represent one of the simplest approaches to preparation of scaffolds applicable in tissue engineering. In this work we investigate preparation of biodegradable polymer fibers based on poly( $\gamma$ -benzyl-L-glutamate) (PBLG). PBLG can be easily functionalized either through modification of glutamate side chains or copolymerization. Side chain nucleophilic substitution with hydroxyamines or diamines reduces the hydrophobicity of the starting polymers and consequently facilitate its enzymatic degradation. Adhesion, proliferation and differentiation of cells on polymer scaffolds thus can be modified by introduction of biospecific peptide sequences exposed on the polymer surface.

We synthesized  $\gamma$ -benzyl-L-glutamate (BLG) homopolymers and its copolymers with more reactive 2,2,2- $\gamma$ -trichlorethyl-L-glutamate (TCEG)<sup>1</sup>, poly( $\gamma$ -benzyl-L-glutamate-*co*-2,2,2- $\gamma$ -trichlorethyl-L-glutamate) (Poly(BLG-*co*-TCEG)). The copolymerization parameters of respective N-carboxyanhydrides were determined according to the Fineman-Ross and Kelen-Tüdös methods. The effect of incorporation of more reactive TCEG ester groups in the polymer chain on the kinetics of its aminolysis with 2-aminoethanol and with propargylamine under various conditions was studied. The conversion of aminolysis of poly(BLG-*co*-TCEG) fibres was calculated from elemental analysis and <sup>1</sup>H NMR. The poly(BLG-*co*-TCEG) fibres were prepared by a solution spinning method from various types of solvent. The effect of solvent on the secondary structure of fibres was study by solid-state <sup>1</sup>H NMR.

**Acknowledgment:** The supported by Centre for Cell Therapy and Tissue Repair (MEYS CR: No.: 1M00216220803) and EXPERTISSUES NoE (NMP3-500283-2) is acknowledged.

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## P 45 - Mon

### **BIOMIMETIC MODIFICATION OF POLYLACTIDE SURFACES THROUGH DEPOSITION OF FUNCTIONAL AMPHIPHILIC BLOCK COPOLYMERS**

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Biodegradable polyesters, such as polylactide (PLA), are important materials in tissue engineering. A specific distribution (pattern) of cell-adhesion structures, e.g. fibronectin-derived peptide sequences (RGDS), over the biomaterial surface is highly desirable in developing materials with controlled cell-biomaterial interactions. Amphiphilic block copolymers composed of polylactide (PLA) and poly(ethylene oxide) (PEO) blocks, containing cell-adhesion fibronectin-derived peptide sequences (RGDS) at the end of PEO block are used in preparation of functional biomimetic surfaces of PLA-based biomaterials, that would facilitate cell migration, growth and differentiation.

The surface topography of the peptide functional groups resulting from the controlled copolymer deposition and the accessibility of peptides on the surface for interaction with proteins, such as cell-adhesion receptors, was studied with copolymers carrying biotin as the adhesion peptide label. The 2D model surfaces were prepared by spin-casting from solutions containing different neutral and functionalized copolymers on PLLA film on a glass support, PLLA film mimicked the surface of real biomaterial. Using biotin as a reporting group, the localization of biotin-labelled copolymer molecules on the surface was accomplished through specific biotin-avidin interaction. Either avidin or avidin-labelled nanoparticles were then visualised by AFM. Both tapping and acoustic mode AFM techniques (AFAM) proved to be convenient methods for characterization of surface topography of functional biomaterials. The effect of spatial surface pattern of biomimetic peptide structures on cell adhesion and growth was demonstrated in cell culture studies.

The support by Academy of Sciences of CR (1QS500110564), Center for Cell Therapy and Tissue Repair (MSMT: 1M0021620803) and 6FP-EU NoE „EXPERTISSUES“ (NMP3-500283-2) is acknowledged.

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### BIOMIMETIC SURFACE BASED ON METAL-POLYMER HYBRIDS PREPARED FROM SELF-ORGANIZED HONEYCOMB FILMS

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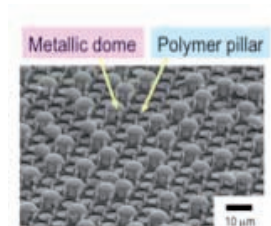
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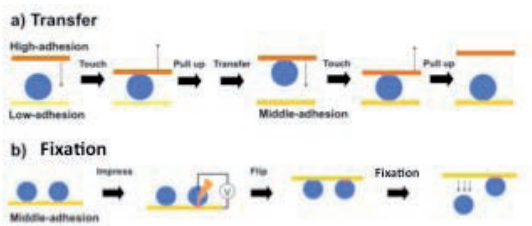
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We have fabricated superhydrophobic metal-polymer hybrid films having strong adhesive force to water droplet, in mimicry of surfaces of gecko feet and rose petals. The hybrid surface was composed of two independent microstructures as shown in Figure 1; hydrophobic hexagonally polymer pillar array and hydrophilic metal microdomes. The pillar array, prepared by peeling of a top layer of a self-organized honeycomb-patterned polystyrene film, shows superhydrophobicity. On the other hand, the metal microdomes formed by nickel electroless deposition is hydrophilic enough to have strong affinity to water droplets. Density of the metal microdomes in the hybrid films was precisely changed from 0 to 30 % by the reaction temperature or the catalytic mixture concentration of the electroless deposition processes. Adhesion property of the hybrid film to water droplets was adjusted by the metal microdome density.

Figure 2 schematically shows two examples of water droplet handling, droplet transfer from lower adhesion surface to medium surface by using the higher adhesion surface as a droplet carrier and droplet fixation by the electric stimulation. Biomimetic approach of controlled wettability is important for material design of superhydrophobic surfaces and their application such as droplet handling in digital microfluidic devices.



**Figure 1.** SEM image of the metal-polymer hybrid film. Dome density is adjusted by preparing conditions.



**Figure 2.** Schematic illustrations of droplet handling on the hybrid film. a) Droplet transfer between two surfaces via the higher adhesive superhydrophobic surface. b) Droplet fixation on the hybrid surface by electric stimulus.

## P 47 - Mon

### COMPLEXES OF CATIONIC POLYMERS WITH ANIONIC LIPOSOMES: STABILITY, STRUCTURE AND PROPERTIES

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Synthetic cationic polymers, poly(N-ethyl-4-vinylpyridinium bromide) (PEVP) and polylysine (PL), were complexed with small unilamellar liposomes ca. 60 nm in diameter, composed of neutral phosphatidylcholine and anionic diphosphatidylglycerol (DFG), a molar fraction of DFG being equal to 0.05.

In both cases, the complexation was accompanied by neutralization of the liposome surface charge and enlargement of particles in the system. The stability of polycation/liposome complexes was dependent on the incubation time. Injection of a salt solution into the complex suspension 5 minutes after the complexation completely removed both PEVP and PL from the liposomal membrane, the aggregates dissociated down to the initial liposomes. However, in 2 hours the salt injection caused PEVP-liposome aggregates to dissociate, but had only slight effect on the size of PL/liposome complex particles. Additionally, the integrity of the liposomal membranes with adsorbed polycations was controlled using liposomes loaded with a NaCl solution. No NaCl leakage was found for PEVP/liposome complex after 2 hour incubation, meanwhile a partial leakage in the case of PL/liposome complex was detected.

The dynamic light scattering showed the formation of an extended PEVP layer on the liposome surface, whose thickness was 25-30 nm in contrast to a 5 nm interfacial layer for PL.

To insight into the complex structure, the cryogenic transmission electron microscopy was applied. The images of PEVP/liposomes complexes demonstrated individual liposomes with the initial sizes; those of PL/liposome complexes contained, together with unchanged liposomes, large shapeless but unilamellar vesicles, obviously resulted from the initial liposome fusion.

The above data allowed the conclusion about a key role of the polycation corona on the liposome fusion. The extended PEVP layer prevented direct contacts of the liposomal membranes that suppressed the liposome fusion. The thin PL layer held liposomes together, but did not meddle in the intraliposomal interactions, that stimulated their fusion.

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### STRATEGIES IN PREDICTING POLYMER NETWORK FORMATION AND STRUCTURE OF COMPLEX SYSTEMS

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Crosslinked polymers applied as engineering or biomedical materials are formed from precursors characterized usually by molecular weight, functionality, composition, and group reactivity distributions. The distributions affect the network formation process and final materials property considerably but sometimes in a way which is difficult even to estimate. The existence of the distributions, sometimes quite wide, makes it difficult to apply any simulation in space. The application of kinetic method is somewhat more manageable but its unsuitability for the description of the gel structure is a drawback. Most suitable are the statistical methods and their combinations which can handle the distributions exactly. Since the network structure is affected by formation history, the derivation of link probabilities (transition probabilities) based on chemical kinetics is a necessary condition. The difference in group reactivities is one of the chemical factors causing a non-random distribution of reaction states of building units and differences in basic network properties. Recently, we found that a random distribution of groups of different reactivity is able to wipe out the reactivity dependent non-randomness.

Two main "physical" factors affect covalent network formation: steric exclusion and cyclization. Cyclization is concerned with any kind of formed cycle before the gel point and elastically inactive cycles after the gel point. Cyclization shifts the gel point conversion to higher values and lowers the concentration of elastically active network chains (EANC). Despite of considerable progress in last decades, it is still difficult to make the simulation of cyclization sufficiently predictive. A semi-experimental method is being developed in which the experimentally determined shift of the gel point conversion is used for determination of the lowering of the concentration of EANCs. The concept is based on rescaling of the dependences on actual group conversion to dependences on intermolecular conversion.

For reversible (physical) gels, formation of a network structure in solvent is essential. The fraction intermolecular bonds and bonds closing cycles are dependent on concentration and temperature (among other factors) and these factors, characterized by binding constant and ring-forming probability, determine the gel point. For equilibrium, the statistical theories serve very well since the memory about gel formation history is wiped out. The physical gels behave as covalent gels only in a certain time window. In true equilibrium, such gels have no equilibrium elastic response. Possible phase separation is associated with gel formation.

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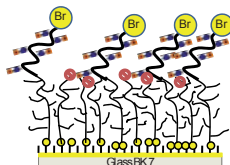
### NOVEL ARCHITECTURE DESIGN OF BLOCK COPOLYMERS OF ETHYLENE GLYCOL METHYL ETHER METHACRYLATE AND CARBOXYBETAINE ACRYLAMIDE

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Growth of polymer brushes from solid substrate is an attractive method for generating robust surfaces with controlled properties and functionalities. The latter is especially important in the design of in real time biosensors where suppression of biofouling is critical. Control in the grafting density has probed to play a very important role in the design of biosensors based on polymer brushes. Higher grafting density results in more protein resistant films, however, polymer brushes with a lower grafting density allow higher levels of functionalization. Therefore engineering surfaces with combined properties of high density and low density brushes is of great interest.

This work aims at developing a method for reducing and controlling the grafting density of a second block of polymer brushes to achieve ultra-low fouling surfaces with an increased capacity for functionalization. A first highly dense poly(monomethoxy capped oligo(ethylene glycol) methacrylate) brush was grafted from a SAM of  $\omega$ -mercaptoundecyl bromoisobutyrate on gold using surface initiated ATRP. A fraction of the living chains were deactivated by modification of Br-chain ends with  $\text{NaN}_3$ . A second block of ultra low fouling carboxybetaine acrylamide (PCBAA) was grafted from the remaining living chains. The different polymer brush architectures allowed us to tailor the density of PCBAA top layer containing carboxy groups exploitable for covalent attachment of biorecognition elements. The chemical composition, wettability, and thickness of the polymer layers were studied by FTIR grazing angle specular reflectance, dynamic sessile water drop contact angle, and spectroscopic ellipsometry, respectively. The swelling behaviour of the brushes was investigated in PBS using ellipsometry. Protein interaction was assessed by challenging the surface with human blood serum and plasma and whole horse serum. A significant decrease in the fouling was achieved for all surfaces.

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### ATOM TRANSFER RADICAL POLYMERIZATION OF MONO-METHOXY CAPPED OLIGO(ETHYLENE GLYCOL METHACRYLATE) IN PHOSPHATE BUFFERED SALINE

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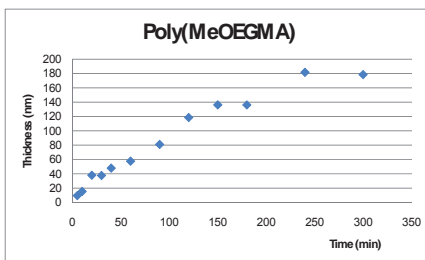
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Covalent attachment of poly(ethylene glycol) (PEG) to proteins can increase their bioavailability and reduce antigenicity. Conventional attachment of PEG chains via reactive chemical groups usually produces a mixture of conjugates with potentially different properties. Recently, some attempts to use atom transfer radical polymerization (ATRP) for grafting PEG from specific protein sites have been described. However, no control in the polymerization was probed. We envision as a possible route for PEGylation well controlled ATRP of oligoethyleneglycol methacrylates. In order to maintain the activity of the proteins all the reaction involving it must be carried out in buffered solutions.

In order to find conditions for controlled ATRP in aqueous protein solutions, we studied ATRP of mono-methoxy terminated oligo(ethylene glycol) methacrylate, poly(MeOEGMA) brushes from a  $\omega$ -mercaptoundecyl bromoisobutyrate immobilized on gold surface using phosphate buffered saline (PBS) as solvent. The chemical composition and thickness of the prepared polymer layers were studied by FTIR grazing angle specular reflectance and spectroscopic ellipsometry, respectively.

The linear increase in the thickness of polymer layer up to 150 nm with polymerization time indicated the control polymerization. The living nature of the polymerization was confirmed by re-initiation of the poly(MeOEGMA) brushes.



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### CRYOGELS BASED ON SYNTHETIC POLY( $\alpha$ -AMINO ACID)s

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In this work, a cryogelation technique were used to create macroporous hydrogels, so called cryogels, based on synthetic poly( $\alpha$ -amino acid)s, poly(AA)s. Due to their polypeptide backbone, synthetic poly(AA)s are cleavable in biological environment by an enzyme-catalyzed hydrolysis<sup>1</sup>. The gels posses key characteristics required for tissue-engineering scaffold materials, such as biocompatibility, biodegradability and open-cell macroporosity.

Cryogels are formed in moderately frozen solutions of monomeric or polymeric precursors<sup>2</sup>. In this process, most of the solvent (water) is frozen and forms ice crystals. While, macroscopically, the sample is frozen, a gel formation occurs in a non-frozen liquid microphase, where the remaining non-freezing components of the system became concentrated. Ice crystals act as a porogen and, after gelation, the system is thawed and a final macroporous structure of the cryogel is formed by swelling.

Briefly, covalently crosslinked gels were formed by a radical polymerization of methacryloylated poly[ $N^5$ -(2-hydroxyethyl)-L-glutamine], PHEG, as a multifunctional macromonomer<sup>3</sup>, at -14 and -19 °C. The concentrations of polymer in water solution were from 2 to 10 % (w/v). Ammonium persulphate and sodium methabisulphite were used as an initiation system. Methacryloylated PHEG (14 mol% MA units, via NMR) was synthesized by polymerization of *N*-carboxyanhydride of  $\gamma$ -benzyl-L-glutamate and subsequent side-chain modification<sup>3</sup>.

Prepared cryogels had a sponge-like structure with pore size in tens of micrometers. When compared with traditional gels, prepared at ambient temperature from polymer solutions with equivalent concentration, some of the cryogels exhibited much better mechanical properties. They were very elastic, the free water present within their pore volume could be repeatedly squeezed out without breaking of the gel and they swell again back to their original shape very fast by capillary effect.

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## P 52 - Mon

### NANOCONTAINERS MADE OF POLYMERIC MESOGLOBULES

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In recent years polymeric nanocontainers have been intensively studied as they can potentially be used in drug delivery systems. The hollow, semi-hollow and core-shell nanoparticles have been obtained [1-3]. One of the most promising method for preparation of nanoparticles containing loose core involves preparation of sacrificial core particles and covering them with polymeric shell. In our previous study the thermosensitive poly(N-isopropylacrylamide) (NIPAM) was used for preparation of core (mesoglobules) particles in aqueous solution above cloud point temperature [2]. These mesoglobules were then covered with a shell via seeded radical polymerization of 2-hydroxyethyl methacrylate (HEMA) in the presence of poly(ethylene glycol) dimethacrylate (PEG-DMA).

Here we present a comparison of mesoglobules obtained from two different thermosensitive polymers: poly(N-isopropylacrylamide) and random copolymers of glycidol and ethyl glycidyl carbamate (P(G-co-EGC)).

First we studied the aggregation behavior of polymers. The polymer concentration had no significant influence on the cloud point temperature of PNIPAM on the contrary to the new thermosensitive (P(G-co-EGC)). In the case of P(G-co-EGC) the transition temperature depends on the number of ethyl carbamate groups introduced into polyether chains [4]. The size of nanoparticles depends on the polymer concentration and heating rate. Additionally the influence of two ionic surfactants: sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) on the size of mesoglobules was investigated.

The nanoparticles prepared without presence of surfactants were used as seeds for the radical copolymerization of HEMA or NIPAM and PEG-DMA as cross-linker. The copolymerization took place on the mesoglobules surface resulting in cross-linked PHEMA shells. The particles formed were monomodal and narrowly distributed as estimated by atomic force microscopy (AFM) and dynamic light scattering (DLS).

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## P 53 - Mon

### EFFECT OF STRUCTURE OF HEMA-DEGMA HYDROGEL MATRIX ON DIFFUSION COEFFICIENTS OF PEG TRACERS

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Diffusion coefficients of paramagnetic polymer tracers in a HEMA-DEGMA copolymer hydrogel matrices at presence of the tracer concentration gradient were measured by One-Dimensional Electron Spin Resonance Imaging (1D ESRI) technique in dependence on polymer concentration in the gel matrix. Paramagnetic tracers were prepared by spin labeling poly(ethylene glycol) (PEG) standards  $M_w = 1500, 3000, \text{ and } 6000$ . Hydrogels in the state close to equilibrium swelling were selected as matrices for diffusion in order to eliminate contribution of the concentration gradient of the solvent to the driving force governing the tracer diffusion. The hydrogels were characterized by concentration of elastically active network chains (degree of crosslinking),  $\nu_{\text{gel}}$ , determined by force-deflection measurement of elastic moduli, by hydrodynamic correlation length,  $\xi_{\text{gel}}$ , determined by dynamic light scattering (DLS), and by self-diffusion coefficient of water in hydrogel,  $D_{\text{H}_2\text{O}}$ , measured by pulsed-gradient stimulated NMR spin-echo (PGSTE).

Experimental dependences of diffusion coefficients on several scaling variables were analyzed in the frame of scaling reptation and hydrodynamic models. Dependences on tracer molecular weight follow expression  $D \sim M_w^x$  with exponent  $x = -1.2 \pm 0.1$  which excludes contribution of reptation to the diffusion. Steep decrease of the tracer diffusion coefficients on polymer concentration  $c$  in these hard gels (concentration range 0.42-0.56 kg/L) was observed. The tracer diffusion coefficients were found to follow stretched exponential function when decreasing with increasing ratio of the hydrodynamic radius of the tracer to the hydrodynamic correlation length of the hydrogel matrix  $R_H/\xi_{\text{gel}}$ . Similarly the tracer diffusion coefficients were found to closely follow stretched exponential dependence on the degree of crosslinking  $\nu_{\text{gel}}$  suggested as a new scaling variable in the whole  $\nu_{\text{gel}}$  range studied.

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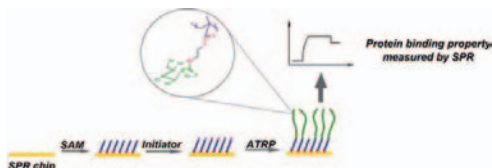
### PROTEIN RESISTANCE OF GLYCOCALYX-MIMETIC GLYCOPOLYMER LAYER: STUDY BY SPR

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Protein adsorption onto the biomaterial surface has been proved to be the first and vital event that initiates subsequent host responses such as blood coagulation, thrombus formation, complement activation, platelet activation and bacterial infection.<sup>1,2</sup> Many efforts have been done to reduce non-specific protein adsorption, and low-fouling surfaces are very useful in many fields such as blood contact device and drug delivery system. The outmost region of cell membrane, called glycocalyx, is constituted by different glycoconjugates.<sup>3</sup> Polysaccharide chains connected to membrane proteins or lipids dominate the cell surface and contribute to the steric repulsion that prevents undesirable non-specific adhesion of other biomacromolecules. It gives us a chance to provide a potential solution to the nonspecific adsorption of proteins.



In this study, we constructed a glycopolymer layer on gold by surface initiated ATRP to mimic the glycocalyx. The glycopolymer chain length was controlled by ATRP reaction time and the chain density was changed by varying the content of functional group (hydroxyl group) ended thiol, which was used for immobilization of ATRP initiator, in the mixture SAM layer. Lysozyme, BSA and fibrinogen were employed to evaluate the anti-nonspecific protein adsorption properties of this biomimetic layer by SPR. The glycopolymer at high grafting density showed significant protein resistance especially to protein with big size. However, due to the abundance of hydroxyl groups which act as hydrogen-bond donors,<sup>4</sup> the glycopolymer also participated in multivalent hydrogen bonding with proteins and showed significant attraction to proteins even in relatively high chain density.

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## P 55 - Mon

### **EFFECT OF EPDM AS COMPATIBILIZER ON MECHANICAL PROPERTIES AND MORPHOLOGY OF PP/LDPE BLENDS**

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Development of new material with broader application is possible by blending polymers, which will give an enhance properties than individual polymer. Producing new materials by blending two homopolymer is economical acceptable, but also from ecological view.

Polypropylene (PP) and polyethylene (PE) represent most of the waste streams, thus a study was focused on preparing and characterization of PP and low density polyethylene (LDPE) blends. Since most of the polymers are incompatible and immiscible, the resulting PP/LDPE blends will exhibit poor mechanical properties as a consequence of low interfacial adhesion. To improve their compatibility ethylene-propylene-diene terpolymer (EPDM) as compatibilizer was added in PP/LDPE blends, in two different amounts (5 and 7 %). Pure homopolymers and PP/LDPE blends with and without EPDM were prepared by extrusion in twin screw extruder. The specimens were prepared by injection molding. Mechanical properties, tensile strength at break, elongation at break, Izod impact strength, were chosen to estimate the compatibilization efficiency of EPDM in PP/LDPE blends. Phase structure and stiffness of PP/LDPE blends with and without EPDM were studied by Dynamic Mechanical Analyzer (DMA). The glass transitions of each component were determined from loss modulus ( $E''$ ) in DMA spectra and interactions between phases were valued through glass transition shifts. The morphology of the blends was investigated by means of scanning electron microscopy.

Tensile strength at break was reduced by adding LDPE to PP. EPDM decreased a tensile strength at break. The higher amount of EPDM did not have influence on tensile strength at break except for PP/LDPE 80/20. For blends PP/LDPE 80/20 and 20/80 the elongation at break was between values of pure homopolymers. Blends PP/LDPE 60/40 and 40/60 had lower values of elongation at break comparing with pure homopolymers. Addition of EPDM improves elongation at break in all blends. The higher amount of added EPDM did not have larger effect of elongation at break value, except in 80/20 blend. Izod impact test showed low values of noncompatibilized blends. PP/LDPE/EPDM blends showed higher Izod impact strength. This effect was more pronounced in LDPE-rich phase blends and with higher EPDM content. Storage modulus ( $E'$ ) was decreased by LDPE addition to PP, as well as by EPDM addition. The shifting of glass transition in PP/LDPE blends with and without EPDM was observed. SEM micrographs of PP/LDPE/EPDM blends showed better compatibility comparing with noncompatibilized PP/LDPE blends.

## P 56 - Mon

### SUPERHYDROPHOBIC AND ANTI-REFLECTIVE NANO-STRUCTURES PREPARED BY SELF-ORGANIZATION AND DRY ETCHING PROCESS

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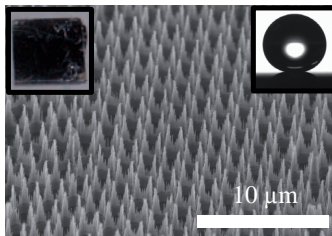
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We have reported that honeycomb-patterned polymer films can be prepared by casting a solution of hydrophobic polymer (e.g. polystyrene, PSt) and amphiphilic polymer on a solid substrate by using condensed water droplet arrays as templates. The pincushion film was formed by simple peeling of the top-layer of the honeycomb-patterned film with an adhesive tape [1]. In this report, we show the preparation of the silicon nano-structures by using self-organized honeycomb-patterned films for masks and dry etching process and their surface properties of wettability and reflectivity. We prepared honeycomb-patterned films from PSt and amphiphilic polymer by the casting method. After UV-O<sub>3</sub> treatment for hydrophilication, honeycomb-patterned films were fixed up side down on silicon substrates with poly(vinyl alcohol) solution as adhesive. After peeling of the bottom layer of the honeycomb-patterned films, pincushion-structured masks were formed on the silicon substrate. After reactive ion etching of the silicon substrate through the mask, the silicon nano-structured substrate was obtained. Figure 1 shows field emission scanning electron microscope image of the silicon nano-structures. Silicon pincushion-like structures with hierarchic spike structures from nano meter to micro meter were formed. Surface reflectance, chemical analysis, and wettabilities of the silicon nano-structures will be discussed.

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**Figure 1.** FE-SEM image of the silicon nano-structures. Insert images show a photograph of the appearance (left side) and a side view of a water droplet on the silicon nano-structure (right side).

## P 57 - Mon

### NEW POLYISOBUTYLENE BASED HYDROGELS PREPARED BY TWO-STEP POLYMER PROCEDURE

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This contribution describes synthesis and characterization of amphiphilic polymer conetworks containing hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA), poly(2,3-dihydroxypropyl methacrylate) (PDHPMA), poly(ethylene glycol) methacrylate (PEGMA), poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA), poly(*N*-isopropylacrylamide) (PNIPAM), poly(*N,N*-dimethylacrylamide) (PDMAAM), poly(methacrylic acid) (PMAA), or poly(acrylic acid) (PAA) and hydrophobic polyisobutylene (PIB) chains. These conetworks were prepared by a two-step polymer synthesis. In the first step, a cationic copolymer of isobutylene (IB) and 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate (IDI) was prepared. The isocyanate groups of the IB-IDI random copolymer were subsequently transformed in situ to methacrylate (MA) groups by a reaction with 2-hydroxyethyl methacrylate. In the second step, the resulting MA-multifunctional PIB-based crosslinker, PIB(MA)<sub>n</sub>, with an average functionality of approximately four MA groups per chain, was copolymerized with appropriate hydrophilic monomer [2-hydroxyethyl methacrylate, 2,3-dihydroxypropyl methacrylate, poly(ethylene glycol) methacrylate, 2-(dimethylamino)ethyl methacrylate, *N*-isopropylacrylamide, *N,N*-dimethylacrylamide, methacrylic or acrylic acid] by a conventional radical process in tetrahydrofuran giving rise to amphiphilic conetworks containing PHEMA, PDHPMA, PEGMA, PDMAEMA, PNIPAM, PDMAAM, PMAA, or PAA and PIB with various compositions. The synthesized conetworks were characterized with solid-state <sup>13</sup>C NMR spectroscopy and differential scanning calorimetry. Amphiphilic nature of the conetworks was proven by swelling in water and heptane.

## P 58 - Mon

### CROSS-LINKED POLY(ASPARTIC ACID) BASED HYDROGELS

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Drug delivery and targeting systems aim to be compatible with the drug and control the rate of its release at the targeted biological disease site with little or no damage to the surrounding tissues. In the development of drug delivery systems, the importance of polymer gels as drug carrier matrices has been already recognised. Hydrogels showing strong and abrupt change in their properties as a response to small changes in the environmental conditions are in the focus. A remarkable volume change in response to pH, temperature, solvent composition or redox potential change is required. Besides the stimuli responsive attribute, biocompatibility and biodegradability of the drug carrier is also important. Polymer gels based on amino acids may fulfil these requirements.

A novel preparation route was developed to synthesise chemically cross-linked poly(aspartic acid) (PASP) polymers and gels. Several natural compounds were selected, e.g., polyamines (putrescine, spermidine and spermine), amino acid derivatives (lysine methyl ester, cystamine) or poly(amino acid) (gelatine) as cross-linkers or poly(succinimide) (PSI). PASP gels were prepared by the hydrolysis of the cross-linked PSI organogels.

The volume of the synthesized non-hydrolyzed PSI gels changed abruptly at a well-defined pH because of ring opening. The hydrolyzed gels showed a reversible volume change around the  $\text{pH} = \text{pK}$  of PASP. The chemically cross-linked PASP gels containing exclusively amino acids were prepared in a chemical synthesis. Similar gels were also prepared using simultaneously two cross-linkers. One of the cross-linkers was insensitive to the variation in environmental conditions while the other could split by certain reagents. Well defined, adjustable swelling of the gels was detected when environmental properties, such as the pH or redox potential, were varied.

This research was supported by the OTKA Foundation (Grant number PD76401) and by the Magyar Zoltán Foundation Postdoctoral Fellowship.

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<sup>2</sup>T. Gyenes, V. Torma, B. Gyarmati, M. Zrinyi: Synthesis and swelling properties of novel pH-sensitive poly(aspartic acid) gels, *Acta Biomater.* 2008; 4; 733-744.



## P 59 - Tue

### **BIODEGRADABLE HYDROGELS FOR SOFT TISSUE ENGINEERING: MICROSTRUCTURE CONTROL THROUGH MICROSYNERSIS**

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We have utilized the polymerization-induced phase separation, microsineresis, as the method to introduce pores into the hydrogel based on dipeptide copolymer with HEMA-monomer crosslinks. This method would be the most simple to control porosity in the hydrogel. However, the thermodynamic conditions have been well studied for rather simple model systems and thus, for the specific chemistry the phase behavior needed to be investigated.

The gels were formed by radical non-linear copolymerization. The polypeptide macromonomer was of the type of methacryloylated poly( $\alpha$ -amino acid): poly[ $N^{\beta}$ -(2-hydroxyethyl)glutamine-*co*-methacryloyllysine] p[HEG-*co*-Ma-Lys]. In terms of the number of methacrylate groups, the macromonomer was multifunctional. The HEMA was used as a minority comonomer to form covalent bridges between macromonomer units. The porosity was the result of microsineresis - i.e. the reaction induced phase separation in the polymerizing system. We studied the effect of chemical composition and water content of hydrogels on the quality and quantity of pores.

The SEM results showed rather isotropic fully communicating pores (mean size 5 – 20  $\mu\text{m}$ ). Such microstructure would allow exchange of nutrients and oxygen during cell cultivation on the hydrogel support. Mechanical properties (shear moduli) and equilibrium swelling of the gels were also characterized. However, the effect of phase separating on mechanical and swelling properties need further investigation before generalization and formulating a model.

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## P 60 - Tue

### FORMATION AND PROPERTIES OF RESPONSIVE DNA HYDROGELS

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DNA hydrogel is a network of chemically crosslinked DNA strands swollen in aqueous solutions. DNA hydrogels can be prepared by the solution crosslinking of DNA using a chemical crosslinker such as ethylene glycol diglycidyl ether (EGDE). Although DNA hydrogels have been prepared by several research groups (1-4), the gelation process of DNA and the viscoelastic properties of the resulting hydrogels have not been reported before.

In the present work, we monitored the gelation reactions of DNA and EGDE in aqueous solutions by classical rheometry using oscillatory deformation tests. Gelation reactions were carried out at various concentrations of DNA, the crosslinker EGDE, and the catalyst TEMED as well as at various temperatures (5). The crosslinking of DNA is characterized by an initial lag phase of about 30 min, followed by a log phase during which the elastic modulus  $G'$  rapidly increases while the viscous modulus  $G''$  decreases. Increasing TEMED concentration in the reaction solution resulted partial denaturation of DNA strands during the lag phase so that stable DNA gels in aqueous solutions were obtained. The heating – cooling cycles of gels and solutions of DNA produced gels exhibiting an elastic modulus in the order of megapascals. Thermoreversible DNA hydrogels were also obtained due to the transition between semidilute and dilute regimes of the same DNA solution depending on the conformation of the DNA chains. The gels obtained exhibited volume phase transitions in aqueous solutions of poly(ethylene glycol)'s of various molecular weight.

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## P 61 - Tue

### TOUGH HYDROGEL BEADS WITH SUPERFAST RESPONSIVITY

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Hydrogel beads have attracted attention as carrier matrices in a wide variety of medical and biological applications, such as affinity chromatography, immobilization technologies, and drug delivery systems [1]. Their response rate and durability still pose some problems in their fields of application. In the present work, macroporous hydrogel beads were prepared by dropwise addition of an aqueous solution of the monomers acrylamide and 2-acrylamido-2-methylpropane sulfonic acid sodium salt into the paraffin oil as the continuous phase at subzero temperatures. The beads prepared between -15 and -20 °C have irregular large pores ( $\varnothing$ ~ 1–10  $\mu$ m), typical for macroporous networks created by the cryogelation technique while nonporous beads were obtained at room temperature via inverse suspension crosslinked method. Swelling measurements show that the low temperature beads swell within seconds to attain their equilibrium states in water. The beads formed at subzero temperatures were very tough and can be compressed up to 94% strain without any crack development while those formed at room temperature were fragile and broke at a strain of about 40% [2].

The results show that tough hydrogel beads formed at subzero temperatures can be used in separation processes in which the separated compounds can easily be recovered by compression of the beads under a piston.

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## P 62 - Tue

### MODELING OF EQUILIBRIUM SWELLING BEHAVIOUR OF POLYELECTROLYTE GELS

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Smart polymer gels can be designed to change swelling degree, elasticity and transport properties in response to externally applied triggers. These gels may have promising applications in controlled drug delivery. In these applications pH-sensitivity has a particular interest.

Polyaspartic acid (PASP) gels were prepared using different polyamines and amino acid derivatives as cross-linkers. These gels exhibited an abrupt change in swelling degree ( $Q_v$ ) at around  $\text{pH} = 4$ .

In our work, a quantitative interpretation of pH-induced swelling is given on the basis of Brannon-Peppas – Peppas theory<sup>1</sup>. The original theory contains several assumptions, in consequence of this it can be applied only in a narrow pH and/or ionic strength interval. Our modified model can be used in almost the whole pH-range. It also means that pH-sensitivity of a given network can be predicted by our modified model. Calculated curve fits well on the measured values in a wide pH-range (Fig. 1). Thermodynamic parameters of different gel systems are obtained by a linear fit<sup>2</sup>.

Our model can be extended to any chemically cross-linked polyelectrolyte gel system since it does not have any assumptions which are specific to our gels.

This research was supported by the OTKA Foundation (Grant number PD76401) and by the Magyar Zoltán Foundation Postdoctoral Fellowship.

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## P 63 - Tue

### A NOVEL GEL ADSORBENT FOR PHOSPHORIC ACID BY TEMPERATURE SWING ADSORPTION/DESORPTION

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The eutrophication of closed water such as lakes, ponds or bays by an influx of phosphorous has become a serious problem. On the other hand, phosphorous is one of the essential elements for life, and should be recovered and reused, as it is a valuable, limited resource. Some methods for the removal or recovery of phosphate from waste water have been proposed. However, the purity of the recovered phosphorous was not high enough to permit its reuse. Thus, the purification of phosphate is needed. Ion exchange is one of the useful methods for purifying the recovered phosphorous, but the regeneration of ion-exchange resins creates new waste and the cost of the regeneration of the resin is high.

In this study, we have developed a novel thermosensitive gel adsorbent for phosphoric acid and investigated their adsorption/desorption properties. The gel adsorbent was made by copolymerization of *N*-isopropylacrylamide (NIPA) and *N,N'*-dimethylaminopropylacrylamide (DMPAA). The adsorbent has a lower critical solution temperature (LCST) and becomes hydrophilic below the LCST. The tertiary amino groups of DMPAA are ionized in water and show a cationic state. As the water content of the gel increases, the equilibrium is shifted to right as expressed below.



Phosphoric acid adsorbed on the ionized tertiary amino groups in the gel network at low temperature. The amount of adsorption increased with decreasing the temperature and/or with decreasing the cross-linker concentration of the gel. Because the ionized tertiary amino groups in the gel increased with an increase of water content of the gel.

On the other hand, the phosphoric acid desorbed from the gel at higher temperature than LCST because of the suppression of ionization of the tertiary amino groups of the gel at lower water content and additional desorption occurred by shrinkage of NIPA chains.

Repeated adsorption/desorption by swinging the temperature was successfully

# P 64 - Tue

## EXPERIMENTAL INVESTIGATION OF THE ANOMALOUS DIFFUSION IN GEL-MEMBRANE SYSTEM

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We present experimental and numerical results on the anomalous diffusion in a membrane system, we estimated the subdiffusion coefficient and anomalous diffusion exponent of the polyethylene glycol 2000 (PEG2000) in agarose gel. The membrane system under study is a cell with three glass cuvettes separated by horizontally located membranes. Initially, we fill the lower and upper cuvettes with the agarose hydrogel solvent while in the middle cuvette there is an aqueous gel solution of transported substance. Then, the substance diffuses from the middle cuvette to the exterior ones through the membranes. Since the concentration gradients are in the vertical direction only, the diffusion is expected to be one-dimensional. The substance concentration is measured by means laser interferometric method. The analysis of the interferograms allows one to reconstruct the time-space dependent concentration profiles of the substance transported from middle cuvette across the top and bottom membranes to the outside cuvettes. The diffusion can be characterised by a time evolution of the so-called near-membrane layer (NML), where the concentration of diffusing substance drops  $k$  times [1]. When the thickness of NML grows in time as  $t^\alpha$  with  $\alpha=0.5$  we deal with normal or gaussian diffusion. If there is a super diffusion and when  $\alpha < 0.5$  we have a subdiffusive behaviour [2]. For each measurement we prepared two gel samples: the pure gel 2% (w/v) water solution of agarose and the same gel dripped by the solute of PEG2000. The initial concentration of solute in the gel was fixed to be 0.00375, 0.0050, 0.0075 and 0.01125 mol/dm<sup>3</sup>. Our results show that thickness of LMN grows in time as  $t^{0.43}$  (with the subdiffusion parameter  $-\alpha=0.43$ ) confirming a subdiffusive transport of PEG2000 in the gel-membrane system and with subdiffusion coefficient  $-D_\alpha = 3.15 \pm 0.08 \cdot 10^{-10} \text{ m}^2/\text{s}^{0.43}$ .

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## P 65 - Tue

### HYDROGELS BASED ON CHITOSAN-POLYVINYLPIRROLIDONE COPOLYMERS FOR DRUG DELIVERY

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Copolymers (Chi-PVP) of modified chitosan (Chi-PM) and vinylpyrrolidone (VP), which can form pH-sensitive hydrogels, were obtained by radical copolymerization. Tert-butylperoxymethyl ester of butendicarbon acid (PM) in Chi-PM, was used as an initiator of VP polymerization, grafting polyvinylpyrrolidone (PVP) onto Chi chains, as well as for cross-linking and forming 3D matrix. Afterwards, samples were washed with distilled water to eliminate non-grafted PVP homopolymer.

During swelling in aqueous solution of cefazolin sodium (CN), Chi-PVP copolymers absorb CN molecules.

It is investigated, that depending on PM content in Chi-PM, equilibrium swelling of hydrogels in CN aqueous solution at pH 4 was 17,5-40,0 g/g Chi-PVP, when in water at pH 4 it was 28,8-44,0 g/g Chi-PVP. At the same time, absorption of CN by Chi-PVP copolymer samples was 130-80 mg CN/g Chi-PVP.

Kinetics of release of pre-loaded in hydrogels CN into water at pH 5 were studied. It is shown that during first 50 hours 22-27% of pre-loaded CN is released (Fig. 1).

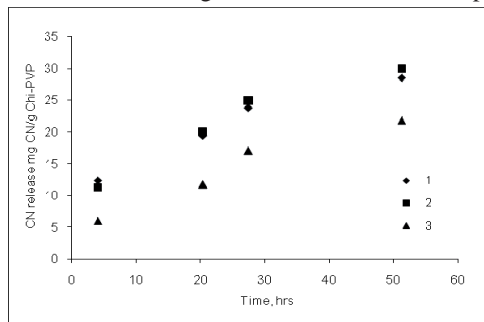


Fig. 1. Kinetics of release of pre-loaded CN from hydrogels, depending on PM content in Chi-PM during synthesis: 1. - 2 kmol/l PM, 2. - 3 kmol/l, 3. - 4 kmol/l.

This proves that above signed hydrogels can be used for creating systems of prolonged drug delivery, and are applicable for bandages to heal wounds and burns, etc.

## P 66 - Tue

### COMPARATIVE ANNEALING STUDY OF PHOTOELECTRIC PROPERTIES OF BULK HETEROJUNCTION ORGANIC SOLAR CELLS BASED ON P3HT:ThCBM[60] AND P3HT:ThCBM[70] BLENDS

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ThCBM[60], a 1-(3-methoxycarbonyl) propyl-1-thienyl-[6,6]-methanofullerene, has been recently used as a thienyl analog of PCBM, in the mixture with P3HT - a poly(3-hexylthiophene-2,5-diyl), with promising results. ThCBM[70] is an analog of ThCBM[60], based on a fullerene with 70 carbon atoms. We have successfully prepared samples of bulk heterojunction organic solar cells based both on P3HT:ThCBM[60] and P3HT:ThCBM[70] mixtures and report on a comparative study of their photoelectric properties in the as-prepared state and after step-wise thermal annealing in the range of 80-180 °C. Thermal annealing is found to be a key step in attaining high efficiency of our cells, similarly as in the already thoroughly studied case of P3HT:PCBM mixtures. Power conversion efficiency of our samples exceeds 2%.

We use the Fourier Transform Photocurrent Spectroscopy (FTPS) to study the optical absorption processes connected with the collection of free photo-generated charge carriers, in the 0.8 - 2.8 eV spectral range. FTPS is very sensitive, its dynamic range reaches 8 orders of magnitude in organic solar cells. FTPS spectra of complete solar cells are complemented with current-voltage characteristics, both in dark and under illumination, and furthermore with UV-VIS absorbance spectra measurements of the active layer alone, undergoing identical annealing steps as the whole cell.



## P 67 - Tue

### **POLYETHER HYDROGELS FROM PHOTO- AND CHEMICALLY CROSSLINKABLE DERIVATIVES OF POLYGLYCIDOL**

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The aim of this work is the synthesis of thermoresponsive networks based upon biologically well tolerable polyglycidol and its derivatives.

By means of coordination polymerization well defined high molar mass polyglycidol was obtained. The hydrophobic modification of hydroxyl groups in polyglycidol led to thermosensitive polymers. The transformation of the hydrophilic hydroxyl groups into hydrophobic ethyl carbamates was used as the tool to achieve control over the thermosensitivity of synthesized polymers. The random poly(glycidol-co-ethyl glycidyl carbamate)s were obtained.

Polyglydol and poly(glycidol-co-ethyl glycidyl carbamate)s were subjected for photo- and chemical crosslinking. For chemical crosslinking hexamethylene diisocyanate was used. Photocrosslinking was achieved by direct UV irradiation of polyglycidol or poly(glycidol-co-ethyl glycidyl carbamate) with photosensitizer added. Alternatively, polyglycidol or poly(glycidol-co-ethyl glycidyl carbamate) was partially esterified with cinnamic acid. UV irradiation of such copolymers led to crosslinking via formation of cyclobutane groups.

Photo- and chemical crosslinking of polyglycidol or poly(glycidol-co-ethyl glycidyl carbamate) led to hydrogels with swelling degree of up to 5000%. The behaviour of the hydrogels as a function of temperature was investigated. At elevated temperature gels become hydrophobic, shrink and release water. The process is reversible. The swelling and shrinking behaviour can be controlled by varying the composition and substitution of the copolymer precursor and by the network density. The obtained hydrogels undergo several swelling/deswelling cycles in response to stepwise changes of temperature.

## P 68 - Tue

### **FAST THERMORESPONSIVE POLY(N-ISOPROPYLACRYLAMIDE) HYDROGELS WITH IMPROVED MECHANICAL PROPERTIES**

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In the presented contribution, we modified our previously developed nanocomposite silica-filled hydrogels with very high response rates to temperature and pH. The aim was to obtain materials with significantly higher moduli, which would be able of strong force response to external stimuli, while keeping the very fast responsivity and the original volume ratio of the swollen and deswollen state. We achieved this goal by synthesizing new gels with thicker pore walls. The amount of silica nanofiller in the new products was optimized. The denser gels were also prepared as nanocomposites with commercial titanium dioxide nanoparticles and hectorite clay. The mechanical properties, the morphology, the kinetics of the volume- and force- response to temperature and to pH will be discussed.

## P 69 - Tue

### **SYNTHESIS AND PROPERTIES OF HYPERBRANCHED POLYIMIDES COMBINED WITH SILICA**

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Aromatic polyimides have become one of the most important class of high-performance polymers. Due to their excellent dielectric, thermal, and mechanical properties, aromatic polyimides have found many applications as high-temperature insulators and dielectrics, coatings, adhesives, and matrices for high-performance composites. Hyperbranched polyimides (HBPI), having highly branched structure and large number of terminal groups, have attracted increasing attention in recent years because they are expected to have unique properties when compared to their linear analogues. Nevertheless, some properties of the polyimides can be also favourably influenced by their combination with inorganic fillers, e.g. silica.

In this work, the amine-terminated HBPI (synthesized by using the thermal imidization of hyperbranched poly(amic) acid based on a commercially available 4,4',4''-triaminotriphenylmethane and 4,4'-oxydiphthalic anhydride in molar ratio 1:1) and series of HBPI-silica hybrid materials via a sol-gel technique and 3-glycidoxypropyltrimethoxysilane used as a coupling agent were prepared.

HBPI-silica containing hybrid films were characterized with respect to their morphology, density, dynamic-mechanical and thermal properties. The influence of silica content and the addition of coupling agent on the structure and properties of the hybrids are also discussed.

Acknowledgement: GA CR 104/09/1357 and MSM 60446137302.

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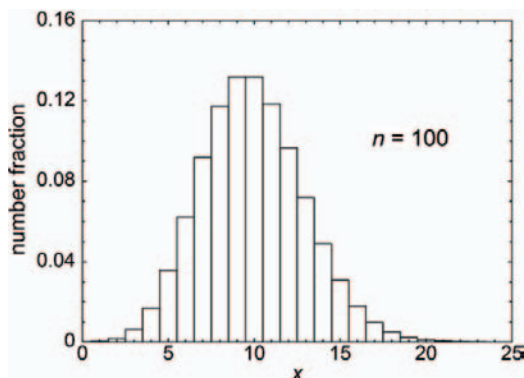
### PROBLEMS WITH TAILORING GRAFT POLYMERS

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The aim of the synthesis of tailored graft polymers is to prepare substances as uniform as possible with respect to molecular weight and degree of grafting. With increasing number of steps in the particular synthesis, the task becomes more difficult and with four or five steps virtually impossible.

The problems are demonstrated by way of example on the five-step synthesis of a graft copolymer with hydrophobic backbone and hydrophilic or polyelectrolyte grafts, viz., poly(4-methylstyrene)-*graft*-poly(methacrylic acid). The five steps are: 1. Synthesis of poly(4-methylstyrene) backbone by anionic polymerization. 2. Partial bromination of the methyl groups. 3. Synthesis of poly(*tert*-butyl methacrylate) living grafts by anionic polymerization. 4. Grafting onto the backbone. 5. Hydrolysis of grafts to poly(methacrylic acid) blocks. In both polymerization steps, a molecular-weight distribution results. In the three chemical-modification steps, there is a distribution of the degree of modification in the individual molecules. Separation of the residues of non-reacted species formed in the preceding step is difficult or impossible. Thus, the final product is multiform mixture of molecules with different molecular weights, chemical compositions and molecular architectures. We estimate that the mass fraction of molecules of the desired substance, i.e., poly(4-methylstyrene)-*graft*-poly(methacrylic acid) in the product is about 0.7 – 0.8. These molecules, however, still differ by molecular weights, degrees of branching and molecular architectures.



The distribution of the degrees of grafting is illustrated by a simplified example of grafting a uniform backbone with degree of polymerization 100 and a desired number of grafts per molecule of ten. The probability,  $p$ , of grafting of any monomeric unit is equal,  $p = 0.1$ . The number fraction of molecules with the desired degree of grafting 10 is only

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### SYNTHESIS AND LIQUID-CRYSTALLINE BEHAVIOR OF TELECHELIC POLY(BUTADIENE)DIOL WITH AZOBENZENE-BASED SIDE CHAINS

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Liquid-crystalline (LC) polymers are attractive materials. Due to their properties, they can be used in photonic, ferroelectric and antiferroelectric applications or in non-linear optics. Introduction of a mesogen into polymer side chains usually leads to the preparation of such polymers. Azobenzene-based mesogens belong to an important class of photochromic materials with properties based on cis/trans isomerization of azochromophore group.

Mesogenic thiols with azobenzene as a rigid part and with various substituent (H-, methoxy-, butoxy- or octyloxy-, Fig. 1) in *para*-position of azobenzene ring were synthesized by multi-step syntheses.

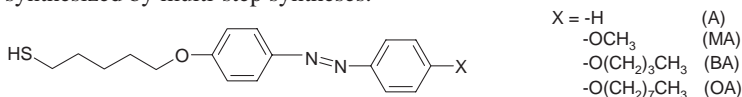


Fig. 1 The synthesized liquid-crystalline units. All of them possess a 1,5-pentane-diyl spacer terminated with thiol group and azobenzene as a rigid, mesogenic part. The thiols designation is written in brackets.

The thiols were grafted onto double bonds of telechelic poly(butadiene)diol ( $M_n \sim 2400$ ; functionality  $f_n = 2$ ; 60 mol. % of 1,2-butadiene units) via radical addition in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN). Initial mole ratio of thiol/double bonds varied in the range of 0.2 to 1.0. Influence of the azobenzene substituent on the extent of modification reaction was estimated using elemental analysis, size-exclusion chromatography and <sup>1</sup>H NMR-spectroscopy.

Using polarization microscopy, temperature-dependent formation of characteristic LC-textures was observed. The detection of the LC-state and mesophase types were confirmed by differential scanning calorimetry and X-ray analysis. It was found that the substituent on mesogen plays an important role in thermal behavior of both the thiols and the obtained comb-like polymers.

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### NANOSTRUCTURED HYBRID MATERIALS PREPARED VIA IN-SITU EMULSION POLYMERIZATION

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<sup>b</sup>*Hexion Speciality Chemicals, a.s., Tovární 2093, CZ-356 80 Sokolov, Czech Republic*

A series of novel polystyrene and poly(butyl methacrylate) montmorillonites nanocomposite latexes have been successfully prepared by emulsion polymerization.

First of all, chemical modification of two types of montmorillonites (Cloisite-Na and Nanocor-Na) with a modifier containing a cationic head with a reactive tail ([2-(acryloyloxy)ethyl]trimethylammonium chloride) has been employed for the synthesis of hybrids. Subsequently, *in-situ* seeded emulsion polymerization of organoclay, hydrophobic vinyl monomers, such as butyl methacrylate and styrene, using sodium dodecyl sulfate and ammonium persulfate as surfactant and initiator, respectively, was used for polymer/clay nanocomposite preparation under monomer-starved conditions. This technique allowed preparing of stable nanocomposite latexes with high (30 – 45 wt.%) solids contents and with loading of inorganic particles up to 5 wt.%.

The prepared wet dispersions were subsequently characterized by light scattering method. Verification of the intercalation of the vinyl monomer-cation within the clay interlayers was achieved by WAXS and SAXS analyses. WAXS patterns taken from polystyrene/organically modified MMTs reveal exfoliated structure for both of used clays. It has been shown that the poly(butyl methacrylate)/organoclay nanocomposites exhibit a better dispersion of disordered clay platelets in polymer matrix films than that of hydrophilic MMT-Na for both of used clays.

#### Acknowledgement:

The authors acknowledge the financial supports of the Academy of Sciences of the Czech Republic (grant KAN 100500651) and of Ministry of Education, Youth and Sports of the Czech Republic (grant ME09058).

### COORDINATION PROPERTIES OF WATER AND POLYMER–WATER INTERACTIONS

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Polymer – solvent interactions, aside from solvent – solvent and polymer – solvent interactions, play an important role in the structure of polymer networks and their macroscopic properties. Vibrational spectroscopy - Raman, attenuated total reflectance Fourier transform infra-red (ATR FTIR) and near-infrared (NIR), and density functional theory (DFT) have been used in a study of water solutions of three tri-block copolymers with commercial name Pluronics. The Pluronic macromolecules (PE6200, PE6400 and F68) associate into micelles in response to increased temperature and they were chosen as a model system for investigation of polymer – water interactions.

Analysis of a hydroxyl stretching vibration region in Raman spectra showed differences between individual Pluronics even at temperatures below the critical micelle temperature. Corresponding region in the ATR FTIR spectra showed that the same water coordination types are present in interacting water as in bulk water. However, the quantitative representation of individual coordination types in the water interacting with a Pluronic macromolecule was dependent on the polymeric chain and temperature. Correlation of current results with literature data on micellar dimensions determined by light scattering<sup>1</sup> and on hydration gradient found by electron spin resonance<sup>2</sup> and correlation with the C-O-C stretching vibration of the Pluronic macromolecules<sup>3</sup> points to the differences in microstructure of micelles formed by the individual Pluronic polymers and subsequent differences in the physical properties of the polymeric chains.

<sup>1</sup> Chu, B. and Zhou, Z. Physical Chemistry of Polyoxyalkylene Block Copolymer Surfactants. In: *Nonionic Surfactants*, Nace, V. M., Ed., Marcel Dekker, New York, **1996**, Vol. 60, 67

<sup>2</sup> Caragheorghopol, A. and Schlick, S. *Macromolecules* **1998**, *31*, 7736

<sup>3</sup> Schmidt, P.; Dybal, J. and Šturcová, A. *Vibrat. Spectrosc.* **2009**, *in press*, doi: 10.1016/j.vibspec.2008.12.003

## SOLID-STATE OXIDATION OF POLYANILINE BASE WITH SILVER NITRATE

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Polyaniline (PANI) is an interesting conducting polymer due to its possible applications. Redox reactions, such as the oxidation of emeraldine form to pernigraniline or its reduction to leucoemeraldine, are important processes in polyaniline chemistry. Solid-state oxidation, *i.e.* the reaction between the PANI base and a solid oxidant, has been reported only rarely in comparison to the solid-state polymerization of aniline or a solid-state protonation of PANI base. In present study, PANI (emeraldine) base was oxidized with silver nitrate. In addition to the understanding of solid-state reactions involving PANI, the preparation of conducting polymer–metal nanocomposites was the goal.

Polyaniline base was ball-milled with an oxidant, silver nitrate, in the solid state. The samples were prepared at various mole ratios of silver nitrate to polyaniline ranging from 0 to 1.5 for various processing times. Emeraldine form of polyaniline was partly oxidized to pernigraniline, and silver nitrate was reduced to metallic silver. Nitric acid is a by-product, which may protonate PANI. FTIR and Raman spectroscopies were used to monitor the changes occurring on the molecular level as the PANI base reacts with silver nitrate.

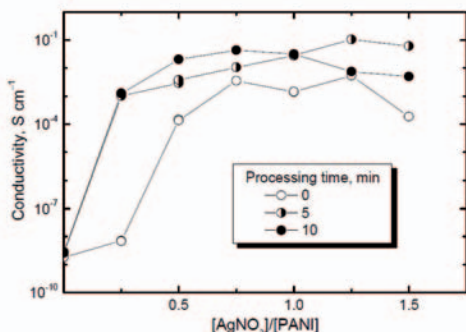


Figure. Dependence of conductivity of PANI base blended with silver nitrate in a ball mill for 0, 5, and 10 min at mole ratios  $[AgNO_3]/[PANI]$ .

The reaction between two non-conducting components, PANI base and silver nitrate, produced a mixture of two conducting components, PANI nitrate and silver. The increase in the conductivity of original base,  $10^{-9}$  S  $cm^{-1}$ , up to  $10^{-2}$  S  $cm^{-1}$  was found, depending on mole ratio of silver nitrate to PANI base and of processing time of components in a ball mill.

<sup>1</sup> Trchová M.; Stejskal, J.; Prokeš, J. *Synth.*



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### EFFECT OF APPLIED ELECTRIC FIELD ON STRUCTURE AND PERMEABILITY OF CHITIN NANOFIBER-REINFORCED CHITOSAN MEMBRANES

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The native biopolymer chitosan is a promising membrane material owing to its good film-forming properties. The tensile strength in an aqueous environment increases and affinity to water decreases if  $\alpha$ -chitin whiskers with nano dimensions (width  $\times$  length 5-70  $\times$  150-800 nm) are incorporated into chitosan phase.

This study concerns the preparation of chitin whisker-reinforced chitosan membranes under the applied homogeneous electric field by the solution casting technique. In membrane preparation, two fractions of commercial chitosan (Aldrich) with the average weight molecular weight (Mw) 536 and 789 kDa with deacetylation degree (DD) 82.6 and 79.0%, respectively, were used. Chitosan was dissolved in 1 % aqueous solution of acetic acid, mixed with concentrated aqueous solution of  $\alpha$ -chitin whiskers (MaviSud Ltd, Italy), cast on a glass plate, which was finally placed between two metal plate electrodes. The electric field (6 and 9 kV) was created by means of a soft power supply PBK4 (Information Unlimited, Inc, USA). At fixed experimental conditions above mentioned, the only variable was the content of chitin whiskers (0.75 - 30 %) in chitosan films. The films with the same compositions were prepared by the tradition casting technique, i.e. without the applied electric field for evaluating its contribution to the composite chitosan film properties.

It was shown that there is the limit of the  $\alpha$ -chitin whisker content, higher which the properties of the composite chitosan films become worse independently whether the electric field was applied during their formation or not. The effects of the applied electric field on structural, mechanical and gas permeable properties of the chitin whiskers-reinforced chitosan films were analyzed and discussed.

#### Acknowledgements

Our thanks are due to the Grant Agency of the Czech Republic for financial support of the study (grant 525/08/0803) and Russian Foundation of Basic Research (grant № 07-03-00177).

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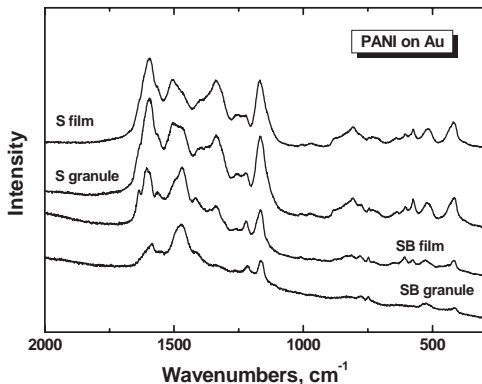
### POLYANILINE FILMS PREPARED *IN-SITU* DURING THE STANDARD AND DISPERSION POLYMERIZATIONS OF ANILINE

Z. Rozlívková<sup>a</sup>, M. Trchová<sup>b</sup>, I. Šeděnková<sup>b</sup>, M. Špírková<sup>b</sup>, J. Stejskal<sup>b</sup>

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Many applications of polyaniline (PANI), such as sensors, antistatic and anticorrosive coatings, require thin films. The technique of *in-situ* surface polymerization, giving rise to thin PANI films, has often been used in the coating of various materials with a conducting polymer overlayer. Thin PANI films prepared by *in-situ* standard and dispersion polymerization [1] on gold and silicon supports in the forms of emeraldine salt and base were at first characterized by atomic-force microscopy, and UV-visible and FTIR spectroscopies. Raman microscope has been used for molecular structure analysis with two different laser excitations at 633 and 514 nm (Figure 1). It has been shown, that the films prepared by dispersion polymerization are thinner, they are more resistant towards the deprotonation by 0.1 M ammonium hydroxide, and they are easily degradable by atmospheric oxygen. In both cases, the films prepared on silicon supports are more stable than those prepared on gold supports.



**Figure 1.** Raman spectra of standard polyaniline films in emeraldine salt (S) and base (SB) forms deposited on gold substrate.

1. Stejskal J., Sapurina I.: Polyaniline: Thin Films and Colloidal Dispersions (IUPAC Technical Report), Pure Appl. Chem. 77, 815–826 (2005).

## P 77 - Tue

### SYNTHESES OF CONJUGATED POLYMERS FOR PHOTONICS

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Conjugated polymers, such as polyphenylenes, polythiophenes, polyfluorenes, fluorene-thiophene copolymers, polycarbazoles, and their modifications have recently attracted great attention due to their potential applications in optoelectronics including light-emitting devices, photovoltaic cells, thin-film transistors, electrochromic devices, and switches. Here the preparation of several special monomers and their conjugated polymers or copolymers will be reported.

By the Suzuki coupling reaction of 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (1) and 3,5-di-tert-butylphenyl 2,5-dibromobenzenesulfonate the alternating poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[2-(3,5-di-tert-butylphenoxy)sulfonyl]-1,4-phenylene} (2) was synthesized. A consequent alkaline hydrolysis of 2 gave a conjugated polyelectrolyte carrying sulfonic groups (3). Monomers 2,5-dibromo-3-[2-(pyren-1-yl)viny]thiophene and 2,5-dibromo-3-[2-(quinolin-4-yl)viny]thiophene were prepared and copolymerized with 1 to get poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[3-(2-(pyren-1-yl)viny]thiophen-2,5-diyl]} (4) and poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[3-(2-(quinolin-4-yl)viny]thiophen-2,5-diyl]} (5), respectively. The conjugated backbone of 4 carries a conjugated pyrene in the side chain and this fluorophore influences the electronic properties of copolymer (4). Consequently the backbone of 5 carries as a spacer the conjugated quinoline structure which can be for instance protonated. By the coupling reaction of 1 and of the prepared methyl 3-(2,7-dibromocarbazole-9-yl)propionate the new poly{[9,9-dioctylfluorene-2,7-diyl]-*alt*-[9-(2-methoxycarbonylethyl)carbazole-2,7-diyl]} (6) was synthesized and utilized as an active layer in organic light-emitting device (OLED).

The utilization of the prepared conjugated polymers can be seen in other posters and papers of our research group.

#### *Acknowledgement*

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### MECHANICAL, DIELECTRIC AND ELECTRICAL PROPERTIES OF POLYANILINE

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Polyaniline (PANI) is one of the important conducting polymers. PANI exists in two fundamental forms: a green, conducting protonated polyaniline and a blue non-conducting polyaniline base. Polyaniline is obtained typically as an intractable powder or, when the polymerization of aniline takes place in the presence of various substrates, as composites. Composites have also been prepared by combining PANI with other polymers, in order to improve the processibility of this conducting polymer. Electrical parameters have always been of prime interest in such materials, even though the mechanical properties may be of importance in many applications.

Mechanical properties of neat PANI have been investigated in the present study. The main problem in the characterization of the mechanical properties of PANI consists in the preparation of suitable samples. The PANI powder obtained after polymerization can only be compressed to produce a solid body, the shape being determined by the press forms available, *i.e.* to pellets. To avoid an influence of the hydraulic pressure on electrical and mechanical properties, a series of "standard" PANI pellets was prepared at different pressures from 100 to 1000 MPa. Mechanical properties were studied on DMA Tritec 2000 apparatus. Conductivity and density of PANI have been determined at ambient temperature. Frequency dependences of the complex permittivity were measured at the wide range of temperatures.

Conductivity, mechanical modulus, and density of the samples are independent of the compression pressure above 300 MPa. All the samples were thus prepared at the 700 MPa, a pressure which has been currently used for the preparation of pellets for the conductivity measurements. Conductivity and Young modulus of the protonated PANI is independent of the acid used for protonation. Activation energy of the AC conductivity depends on the protonating acid.

**Acknowledgement:** Financial support of Ministry of Education, Youths and Sports of the Czech Republic (MSM 0021620834 and 0021620835) is gratefully acknowledged.

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### **LIQUID POLYBUTADIENES - INFLUENCE OF MODIFICATIONS ON SOME PHYSICAL PROPERTIES.**

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We measured densities and surface tensions of a set of differently maleated and one non-substituted polybutadienes and of another commercial hydroxyl-terminated polybutadiene. For the latter, we found some inconsistency in data and even apparent increase in surface tension with growing temperature about which might be in fact caused by high dynamic component of surface tension. Therefore we tried to compare properties measured on the first mentioned non functionalised sample with some other non functionalised polybutadienes, properties of standard commercial sample with the sample with extra low content of residual solvent, and to measure the time dependence of dynamic surface tension of some samples.

Some differences between the standard sample and the sample with low content of residual solvent were expected, but they were found stronger than differences between functionalized polybutadienes. Density of non functionalised polybutadiene taken additionally for comparison is by nearly 1 % lower than density of equivalent material of original series. Density of OH-terminated polybutadiene with extra low content of residual solvent is again by more than 0.5 % lower than density of standard commercial sample of the same PBD. Since the most difference in the original series of materials is about 5 %, comparison of properties between PBDs of different series will bring some information, but it can be treated as qualitative only. The dependence of surface tension on functionalisation is more complicated and was presented in detail elsewhere. The surface tension of OH terminated PBD with extra low residual solvent content was by up to more than 10% higher than that of standard sample, what is more than difference caused by functionalisation. The dynamic component of its surface tension is more than 6 mN/m at 80 °C, where the static surface tension (after several hours) appears to be about 24 mN/m, therefore the time dependence complicates comparison between samples.

This work was supported by the project AVOZ 40500505.

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### **GLYCOLYSIS OF POLYURETHANE FOAMS UNDER MICROWAVE HEATING CONDITIONS**

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Polyalkene, polyether, polyester and polycarbonate based flexible polyurethane (PUR) foams were prepared and consequently chemically decomposed by means of glycolysis using classical and microwave heating. The aim of work is to study an influence of different chemical structure of the PUR foam on depolymeration reaction rate under microwave irradiation and a comparison of microwave heating glycolysis with the classical one. Dipropylene glycol (DPG) (PUR / DPG weight ratio 1 / 1) and diethanolamine were used as a glycolytic agent and a catalyst, respectively. Foam dissolution times were compared and glycolytic products were studied by viscosity measurement. Dissolution time of the polyalkene based PUR foam decomposed by microwave was 4times shorter than in the case of conventional heating and for the polycarbonate based PUR foam the dissolution in the microwave reactor was even 5.6times faster. A complete decomposition of the polyalkene based PUR foam (indicated by viscosity measurement) took 190 minutes when conventional heated, while 25 minutes only was needed for used microwave heating conditions. The products (decomposed PUR foams) were further analyzed (SEC, FTIR) and the mechanism of the PUR depolymerization under microwave field was also discussed.

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### **BIOSORBENTS FROM RICE STRAW PREPARED BY MICROWAVE HEATING**

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Rice straw was chemically modified by phosphorylation using conventional heating or microwave heating. Rice straw, which was pretreated by NaOH solution gave the highest phosphorus content when it was phosphorylated by MW at 450 W (7.07%P, ion exchange capacity 2.60 meq/g). By the reaction at 150°C for 3 hours in oil bath, the modified rice straw had phosphorus content of 6.319% but higher ion exchange capacity than that of microwave heating (2.994 meq/g).

The feasibility of the modified rice straw as cation adsorbent for removing heavy metal from aqueous solution was investigated.  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$  were used as sorbates. In sorption test of 40 ppm with 2.0 g/L of the modified rice straw, both modified rice could adsorb ion metals better than the commercial ion exchange resin (dowax) at the time less than 60 min, and performance of modified rice straw from MW reaction was comparable to dowax for the long time adsorption. In spite of lower ion exchange capacity, the modified rice straw prepared by microwave heating (A-MW2) showed greater adsorption ability than modified rice straw prepared by oil baht (A-O2). Almost 90% of  $\text{Cd}^{2+}$  and  $\text{Cr}^{3+}$  were removed after 60 minutes and it removed 99% of  $\text{Pb}^{2+}$  after 30 min.

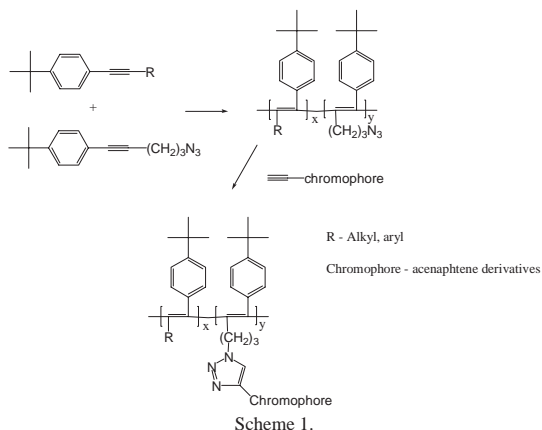
Microwave heating gave modified rice straw which have greater ability adsorption than the conventional heating. Furthermore, The reaction by microwave heating can save time and cost for preparation. The result suggested that modified rice straw, which is biodegradable can be one of alternative ion exchange resin.

## APPLICATION OF “CLICK” CHEMISTRY FOR POST-POLYMERIZATION MODIFICATION OF DISUBSTITUTED POLYACETYLENES

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Conjugated polymers derived from substituted acetylenes such as poly(vinylene)s, poly(arylenethynylene)s, poly(arylene-enyne)s, polymers formed by polycyclootrimerization, etc. attract great attention due to their potential applicability in various fields of electronic, optoelectronics and nonlinear optics. Particular attention in this field is devoted to disubstituted polyacetylenes and polymers with heterocycles either in the main chain or as pendant groups. Here we report statistical copolymers of 1-(*t*-butyl-phenyl)-2-( $\alpha/\beta$ -naphthyl)acetylene with various “active” group bearing co-monomers (see Scheme 1). Postpolymerization modification by various heterocyclic chromophores using 2+3 copper catalyzed Huisgen type cycloaddition (“click” chemistry) allows further copolymer properties tuning.



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### **SYNTHESIS AND CHARACTERIZATION OF POLY(PHENYLENE OXIDE) GRAFT COPOLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATIONS**

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A series of comb-like poly(phenylene oxide)s (PPO) graft copolymers with controlled grafting density and length of grafts were synthesized by atom transfer radical polymerization (ATRP). The  $\alpha$ -bromo-poly(2,6-dimethyl-1,4-phenylene oxide)s (BPPO) were used as macroinitiators to polymerize vinyl monomers and the graft copolymers carrying polystyrene (PS), poly(*p*-acetoxystyrene) (PAS), and poly(methyl methacrylate) (PMMA) as side chains were synthesized and characterized by NMR, FTIR, GPC, DSC and TGA. The composition-dependent glass transition temperatures ( $T_g$ ) of PPO-*g*-PS exhibited good correlation with theoretical curve in Couchman equations except for the cases of low PS content (< 40 mol %) copolymers in which a positive deviation was observed due to enhanced molecular interactions. The increase in monomer/initiator ratio led to the increase of degree of polymerization and the decrease of polydispersity. Despite the immiscibility nature between PPO and PMMA, the PPO-*g*-PMMA exhibited one single  $T_g$  in a wide temperature window throughout various compositions indicating a complete segmental mixing on a molecular scale due to grafting structure.

## P 84 - Tue

### PHOTOPOLYMER FOR OPTICAL HOLOGRAPHY AND HOLOGRAPHIC INTERFEROMETRY

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Photopolymers are attractive recording media for different holographic applications such as diffractive optical elements, holographic memories, or holographic interferometry. They enable complex wave fields recording without an additional wet chemical developing process, because a hologram is formed already during exposition due to a light induced polymerization (e.g. [1],[2]). In our laboratory, we have prepared and tested acrylamide-based photopolymer recording material. Nowadays, we have started to apply this acrylamide-based photopolymer in holographic interferometry [3]. This technique can be used for measurements of displacements of an object or it can detect optical path deviations in transparent materials with a very high precision. The measurements can be applied to stress, strain and vibration analysis, as well as to non-destructive testing. Interferograms produced on photopolymers are formed in situ and without wet chemical developing process which is their big advantage. With our photopolymer, we have successfully acquired time average interferograms of vibrating piezoelectric elements with various vibration modes.

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- [3] P. K. Rastogi: Holographic Interferometry: Principles and Methods, Springer-Verlag, Berlin, 1994

### **GELS AND XEROGELS OF P(VDF-TFE) COPOLYMER WITH PROPYLENE CARBONATE<sup>1</sup>**

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One of the effective ways of supermolecular structure formation is realization of controlled phase separation in polymer solutions. In this case conditions of the phase separation define morphology of polymer structure in the range from fine dispersed to coarse heterogeneous. An important step on the way from liquid to solid state is gel phase – three dimensional network with junction of different nature. Gel network enable to fix and keep the structure obtained in phase separation during other stages of removing or extraction of the solvent. Thus thermoreversible gels make possible to obtain different types of materials from different membranes to high-strength fibers using gel-technology.

Recently gels based on poly(vinylidene fluoride) and its copolymers are of the high interest because they could use on the one hand as a chemically inert micro-filtration and ultra-filtration membranes for fine separation processes on the other hand as a solid polymer electrolyte in lithium ion cells.

The aim of the work was to establish gelation regimes of system P(VDF-TFE) – propylene carbonate and determine relationship between regimes of gelation and structure of the obtained xerogels (gels without solvent) and their properties.

In the work fragment of phase diagram P(VDF-TFE) – propylene carbonate was plotted. The regions of solution concentration and temperature which make sure phase separation were determined using oscillatory rheology techniques. The relationship between conditions (temperature) of gel formation and supermolecular structure of respective xerogels was specified at different levels (WAXS, SEM).

Mechanical properties of oriented and unoriented xerogels in comparison with P(VDF-TFE) films obtained by usual solvent techniques was tested. It was shown that maximal uniaxial draw ratio of P(VDF-TFE) xerogels is 1.5 – 2 times higher than that of P(VDF-TFE) films obtained by usual solvent techniques and it makes possible to increase mechanical properties.

## P 86 - Tue

### **RHEOLOGICAL BEHAVIOUR OF SWOLLEN HYDROGELS**

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We studied rheological properties of covalently cross-linked polymer hydrogels based on 2-hydroxyethyl methacrylate. A model series included samples of different morphology: homogeneous and phase-separated gels with or without communicating pores. Samples microstructure was tested by environmental scanning electron microscopy and phase contrast light microscopy.

In this project we targeted to develop approaches to accurately determine mechanical properties of both homogeneous and porous hydrogels using a contemporary version of rotational rheometer Bohlin HR Nano. Conducting both rheological and structural studies on the same samples encouraged us to seek for a connection between hydrogel morphology and its rheological properties.

We determined Young's modulus, equilibrium elastic shear modulus, and dynamic linear viscoelastic shear properties of gels. For soft non-flowing swollen materials choice of compression state was extremely important to get meaningful rheological characteristics. Conditions of methodologically correct measurements were defined.

Thus, shear properties independent of measurement conditions were evaluated for hydrogels of various morphologies. Analyzing all the rheometry results in complex, we were able to distinguish between porous and non-porous gels, in other words, to "sense" the microstructure rheologically.

*Authors acknowledge support of this work from the DuPont De Nemours Company (DuPont Young Faculty Award for MD)*

## P 87 - Tue

### OVERLAP IN POLY(ACRYLIC ACID) AQUEOUS SOLUTIONS IN ACIDIC MEDIUM<sup>1</sup>

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Equilibrium and dynamic characteristics of polymer solutions, as well as macromolecular reactions mechanism and their product properties are highly dependent on the concentration regime. Key characteristics of concentration regime are crossover concentration  $C^*$  (dilute-semidilute solution transition) and concentration of entanglements formation -  $C_e$ . Recently it was proved that poly(acrylic acid), PAA may interact in acidic media with various polycations forming temperature-sensitive complexes due to ion-dipole interactions. Thus, it is necessary to study concentration regimes of PAA solutions in presence of mineral acid (HCl) at different temperatures.

Experiments included dynamic (DLS) and static (SLS) light scattering, and capillary viscometry at HCl concentrations of 0.1-0.2 M in a wide range of temperatures.

It was shown that  $C^*$  as calculated from inverse intrinsic viscosity decreases with increasing temperature, as solvent thermodynamic quality was improving. The data is in good agreement with temperature dependence of PAA coils hydrodynamic radius (derived from diffusion coefficient). At the same time  $C^*$  values obtained from DLS data (according to appearance of cooperative diffusion) and SLS are in good match, and both do not show any temperature dependence.

Our results revealed that extrapolation to zero concentration describes well properties of isolated macromolecules, but it is restrictedly applicable to the overlap area, due to neglecting interchain interactions.

$C_e$  was determined from flow mechanism change in capillary viscometry studies.  $C_e$  (~ 4%) and  $C^*$  (~2.5-3%) values are very close, and concentration dependence of viscosity is typical for non-charged macromolecules solutions.

From temperature dependence of viscosity thermodynamical parameters of flow were derived. It was shown that concentration dependencies of viscous flow enthalpy  $\Delta H_v$  have minima in the vicinity of  $C^*$ , and its depth increases as HCl concentration grows. These results are in accordance with theoretical and experimental data on extremal character of  $\Delta H_v$  concentration dependence in poor solvents, and considerably expand them.

## P 88 – Tue

### FIRE-RESISTANT AROMATIC POLY(ARYLOXYSILOXANES)

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Bisphenols were converted to their respective poly(arylsiloxanes) to assess the influence of the organic unit on fire retardancy. These included (1) bisphenols having characteristic isopropylidene bridging unit between aryl rings, namely, 2-(4'-hydroxyphenyl)-2-[4'-(4-hydroxyphenyl)phenyl]-propane (triBPA)<sup>1</sup> with three aryl rings, and bis[4-(4'-hydroxyphenyl)phenyl]propane (TABPA)<sup>2</sup> having four aryl rings, (2) polyphenyls lacking the isopropylidene bridging unit, namely, 4,4'-dihydroxybisphenyl (DOD) and 4,4''-dihydroxy-*m*-terphenyl (MTP), and (3) 4,4'-bishydroxydeoxybenzoin (BHDB). The latter compound has recently been utilized in the synthesis of polyarylates and polyphosphonates<sup>3,4</sup> which exhibited excellent flame-resistant properties, with heat release capacity data (HRC) <100 J/g.K, and char yields of 45-50 %. Flame-resistant properties of these materials were investigated by TGA and pyrolysis combustion flow calorimetry (PCFC) to measure heat release capacity (HRC) and total heat release (THR). TGA studies revealed high char yields (30 - 50%). Low to moderate flammability was demonstrated by HRC values of 45-250 J/g.K. Poly(aryloxysiloxane)s based on BHDB, MTP, and DOD had exceptionally low HRC values (45, 85 and 120 J/g.K respectively) and high char yields (~50%) making them promising candidates for potential applications as a flame retardant materials.

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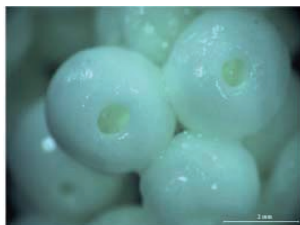
## P 89 - Tue

### SINGLE-HOLE MACROPOROUS ORGANOGEL PARTICLES OF HIGH TOUGHNESS AND SUPERFAST RESPONSIVITY

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Hollow polymer particles or microcapsules are of technological importance in controlled release of drugs, cosmetics or, in the removal of pollutants. In this study, we introduce a simple strategy that allows the preparation of millimeter-sized macroporous organogel particles with a polydispersity of less than 10%, containing a single large hole in their surfaces (Figure 1). These particles were prepared by solution crosslinking of butyl rubber (PIB) in benzene using sulfur monochloride ( $S_2Cl_2$ ) as a crosslinking agent. The reactions were carried out within the droplets of frozen solutions of PIB and  $S_2Cl_2$  at  $-18^\circ C$ .



**Figure 1.** Optical microscopy images of PIB beads formed at  $-18^\circ C$ .  $S_2Cl_2 = 20$  v/w %. PIB concentration = 10 w/v%. The scaling bar is 2 mm.

The particles display a two phase morphology indicating that both cryogelation and reaction-induced phase separation mechanisms are operative during the formation of the porous structures. The beads exhibit moduli of elasticity of 1–4 kPa, much larger than the moduli of conventional nonporous organogel beads formed at  $20^\circ C$ . The gel particles also exhibit fast responsivity against the external stimulus (solvent change) due to their large pore volumes (4–7 ml/g). The gel beads prepared at  $-18^\circ C$  are very tough and can be compressed up to about 100% strain during which almost all the solvent content of the particles is released without any crack development.

Tuncaboylu, D.C, and Okay O, *Eur. Polym. J.* (2009)

## P 90 - Tue

### HYBRID MACROMOLECULAR ANTIOXIDANTS: SYNTHESIS, PROPERTIES AND APPLICATION IN MEDICINE.

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At the present time, the capability of antioxidant application for the correction of a variety of pathologies arising at the distortion of physiologic lipid peroxidation was verified both experimentally and theoretically. Now, the chemistry of phenol antioxidants reached its apex and simple variation of molecular elements does not gain a significant change of antioxidant effectiveness.

Thereby it is very perspective to synthesize hybrid macromolecular antioxidants combining in structure valuable macromolecular and antioxidant properties. New approaches have been developed for the chemical modification of such polymers<sup>1</sup>. Synthesized hybrid antioxidants can be varied in terms of molecular mass, the content of antioxidant and the nature of antioxidant-polymer covalent bond<sup>2</sup>. For this purpose hydrophilic bio- and synthetic polymers were used together with some derivatives of sterically hindered phenols. Hydrophilic-hydrophobic balance which is sensitive to the presence of antioxidant attached to a polymer backbone allows controlling solubility in a variety of solvents. One of the ways to exploit the unique properties of the synthesized compounds is their utilization in blood plasma replacement solutions that demands deeper understanding of hybrid antioxidants behavior in aqueous systems. By means of DLS, TEM and fluorescence spectroscopy methods, the molecular properties of the hybrid antioxidants were investigated. It was established that in water single macromolecules coexist with aggregates those concentration, however, is negligible in comparison with single molecules<sup>3</sup>.

On the basis of the hybrid macromolecular antioxidants new types of blood plasma replacement solutions are developed (Patent № 2273483, 2005)

The tests on laboratory animals proved that the designed hybrid macromolecular antioxidants were acting as a blood plasma substituent and as an antioxidant. The increasing of the survivorship rate by two orders of magnitude at conditions of acute hemorrhage was observed.

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## P 91 - Tue

### **SURFACE PROPERTIES OF POLY(VINYL ALCOHOL) WITH IRON CHLORIDE (III) BEFORE AND AFTER UV-IRRADIATION**

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Different additives are used in producing of polymers to obtain suitable properties of plastics. These additives may influence photodegradation of the polymers.

The aim of this work was to study of the surface properties of poly(vinyl alcohol) (PVA) in the presence of iron chloride (III) before and after UV-irradiation.

Poly(vinyl alcohol) 87-90 % hydrolyzed with average mol. wt. 30,000-70,000 and iron chloride (III) reagent grade, 97%, were purchased from Sigma-Aldrich.

Thin polymeric films of poly(vinyl alcohol) with different content of FeCl<sub>3</sub> (1, 5 wt.%) were UV-irradiated in air atmosphere. Intensity of incident light was 19.5 mW/m<sup>2</sup>.

Changes in the surfaces were investigated by measurements of contact angles and atomic force microscopy (AFM). Surface free energy and its polar and dispersive components were calculated on the basis of measurements of glycerol and diiodomethane contact angles.

Measurements of contact angles and calculations of surface free energy pointed out that addition of 1% of FeCl<sub>3</sub> to poly(vinyl alcohol) makes the surface more hydrophilic; whereas, addition of 5% of FeCl<sub>3</sub> to PVA makes the polymer surface more hydrophobic in comparison with pure PVA. It suggests that iron chloride (III) affected surface structure of PVA. In the presence of 5% of FeCl<sub>3</sub> hydroxyl groups from PVA accumulated beneath the surface but in the presence of 1% of FeCl<sub>3</sub> these groups were on the PVA surface.

UV-irradiation caused the decrease in values of glycerol contact angles and increase in surface free energy and its polar component, which was connected with appearing of polar groups on the sample surfaces. The highest drop in value of glycerol contact angle was observed for PVA containing 5% of FeCl<sub>3</sub>, whereas the lowest change was found for pure PVA. Iron chloride (III) might deliver chlorine atom and facilitate photooxidation of the polymer.

The polymer surfaces studied by AFM methods were flat, especially these with iron chloride (III). Roughness parameters ( $R_a$ ,  $R_q$ ) were very small, for PVA  $R_q$  was 3.05 nm, for PVA with 1% of FeCl<sub>3</sub> - 1.06 nm and for PVA with 5% of FeCl<sub>3</sub> - 1.08 nm.

After UV-irradiation surfaces studied changed little - holes and hills appeared. Roughness parameters ( $R_a$ ,  $R_q$ ) increased insignificantly. Changes in the polymer surfaces were caused by photooxidation and photodegradation of PVA.

## P 92 - Tue

### **NANOINDENTATION STUDIES OF POLY(METHYL METHACRYLATE) DOPED WITH PHOTOINITIATOR**

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Studies of nanomechanical properties of polymers and plastics are very important in case of fabrication of miniaturised devices for various applications, e.g. in production of sensors for detection of pollutants in environment or in medical diagnostic. Nanohardness can be studied by Atomic Force Microscopy using indentation mode.

The aim of our work was to estimate the nanohardness of poly(methyl methacrylate), PMMA, which was physically modified by introduction of small amount (5% m/m) of commercial photoinitiator. Thin polymeric films of origin and doped PMMA were exposed to UV-irradiation source for surface modification and then analysed by Atomic Force Microscopy (MultiMode, Veeco). The three-sided pyramid diamond cantilever with 60 degrees apex angle was used for nanoindentation test. The force-distance curves were recorded and the hardness of sample was calculated on the base of the dent size analysis. The idea of nanohardness measurement by AFM is similar to the well-known macroscale techniques. However, the nanoscale tests provide an information in detail chosen point of thin top layer.

The following simple formula is applied for hardness calculation:

$$F = k \cdot x, \text{ (N)}$$

where  $k$  is the spring constant (expressed in N/m) and  $x$  is the cantilever deflection. The precise value of spring constant needed to calculation of material hardness was obtained by application of original method elaborated at our university. Besides of hardness measurements the imaging of modified sample surface was done by AFM. The discussion of effects of UV-irradiation and photoinitiator added to polymer film on sample nanohardness and morphology was supported by the spectroscopic results.

## P 93-Tue

### PREPARATION AND CHARACTERIZATION OF POLY(ASPARTIC ACID)-GELATIN CO-NETWORKS

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Controlled and targeted drug delivery systems play an increasing role in today's pharmaceutical researches. These systems are capable of releasing blocked drug molecules only on targeted areas which decreases the unnecessary loading and toxic side-effects in body.

The main activity of our research group is developing amino acid based polymer gels as novel drug delivery systems. The application is based on their unique properties: these materials do not represent loading to the environment and the human body because i) they are presumably biocompatible due their monomer units and ii) their enzymatic degradation yields harmless molecules.

Poly(aspartic acid) based gels developed by our group exhibit an abrupt change in swelling degree and other properties when the pH in their environment is modified. This phenomenon enables these systems to be applied in pH-induced drug delivery<sup>1</sup>. As a new synthetic route, we have designed gel structures in which gelatin macromolecules establish chemical cross-links between polymer chains instead of small molecules. These co-networks have the physical and chemical properties of both poly(aspartic acid) and gelatin.

The elastic modulus has been studied as a function of gel constitution i.e. the gelatin molar ratio in the network. The influence of pH, solvent quality and temperature on elastic and swelling properties were investigated in details.

This research was supported by the OTKA Foundation (Grant number PD76401) and by the Magyary Zoltán Foundation Postdoctoral Fellowship.

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## P 94 - Tue

### OPTIMIZING CONDITIONS FOR FUNCTIONALIZATION OF PLGA-PEG-PLGA COPOLYMER WITH ITACONIC ANHYDRIDE

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In recent years, stimuli-sensitive polymers with specific response to various external stimuli such as pH, electric field, temperature, and other stimuli have been investigated for biomedical application, especially in drug delivery systems, tissue engineering and medical devices.

In this work, temperature-sensitive PLGA-PEG-PLGA triblock copolymer was prepared via ring opening polymerization method in a bulk using stannous 2-ethylhexanoate as catalyst under the nitrogen atmosphere. Resulting well-defined copolymer was subsequently modified by itaconic anhydride (ITA), which brings reactive double bonds and carboxylic acid groups to both ends of the copolymer. Final multifunctionalized biodegradable ITA/PLGA-PEG-PLGA/ITA copolymer is pH sensitive and can be cross-linked either by covalent bonding or by ionic interactions.

Optimization of ITA functionalization conditions were evaluated by the effect of ITA purification, temperature, time and presence of solvent. Successful end-capping of ITA to the end of PLGA-PEG-PLGA copolymer was precisely characterized by means of <sup>1</sup>H NMR, FT-IR and GPC methods. Optimal conditions for synthesis of ITA/PLGA-PEG-PLGA/ITA copolymer were reached with sublimated itaconic anhydride in a bulk, at temperature of 110 °C with total time of 1.5 hours, when 68.7 mol.% of ITA was end-capped to the original PLGA-PEG-PLGA copolymer. Higher temperature resulted in broader polydispersity index along with lower molecular weight predicated polymer degradation, longer time had no effect on the better end-capping, lower temperature and solvent addition significantly reduced or even suppressed the ITA functionalization. Purification of ITA by sublimation prior the use increased the yield of end-capped ITA.

## P 95 - Tue

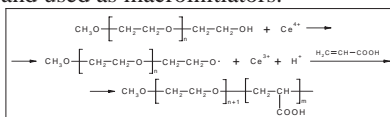
### SYNTHESIS AND CHARACTERIZATION OF DOUBLE-HYDROPHILIC BLOCK COPOLYMERS BASED ON MONOMETHYL ETHER OF POLY(ETHYLENE OXIDE) AND POLY(ACRYLIC ACID) WITH THE DIFFERENT BLOCK LENGTHS

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Double-hydrophilic block copolymers composed of two water-soluble blocks of different chemical nature are perspective polymer materials. Their chemical structure may be tuned for a wide range of applications covering as different aspects as stabilization of colloids, induced micelle formation, polyelectrolyte complexing and complexing by hydrogen bonds towards novel drug delivery system. At the same time, the double-hydrophilic block copolymers with the system of cooperative hydrogen bonds between proton-donor blocks such as carboxylic polyacids and proton-acceptor blocks such as poly(ethylene oxide) or its ethers are of special interest.

In the present work double-hydrophilic block copolymers consisting of poly(acrylic acid) charged blocks (PAAc) and neutral blocks of monomethyl ether of poly(ethylene oxide) (MEPEO) are synthesized by free radical block copolymerization of PAAc with monomethyl ether of poly(ethylene glycol) (MEPEG) of different molecular weight ( $M_{vMEPEG}=1.1 \cdot 10^3 - 5 \cdot 10^3$ ), which were activated by  $Ce^{IV}$  ions and used as macroinitiators.



It was revealed that the block copolymerization process has a matrix character because non-covalent interactions of propagating PAAc chains with MEPEG. This fact points out the formation of intramolecular polycomplexes (IntraPCs) in the given diblock copolymers. Existence of IntraPCs in MEPEO-*b*-PAAc and its behavior with varying degree of ionization of the PAAc block was investigated by the method of potentiometric titration. The self-complexation of MEPEO-*b*-PAAc copolymers under varying pH is considered. The critical concentration and the value of the Gibb's free energy of MEPEO-*b*-PAAc micelle formation at pH=3 were calculated. The characterization of diblock copolymers MEPEO-*b*-PAAc carried out by  $^1\text{H}$  NMR spectroscopy fully confirmed its chemical structure and allowed finding the  $M_{n\text{PAAc}}$  and  $M_{n\text{MEPEO-}b\text{-PAAc}}$

## P 96 - Tue

### MODELING THE MOLECULAR RECOGNITION OF NUCLEIC ACID BASES BY POLYMERIC RECEPTORS

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Komiyama et al. described that poly(2-vinyl-4,6-diamino-1,3,5-triazine) (PVDAT) could efficiently recognize nucleic acid bases and their derivatives. The different recognition in water [1] and methanol [2] was attributed to changes in the microenvironment around DAT residues, which disfavors the formation of hydrogen bonds and promotes stacking interactions in the case of water, while the opposite trend holds in methanol solutions. In the absence of any direct structural information, molecular modeling can be usefully applied to analyze the factors contributing to the stabilization of the complexes formed between PVDAT and nucleobases or related compounds. Thus, the system was approximated by the DAT trimer and three guest molecules, and using the RI-BP-D/SVP quantum chemical method (see ref. [3]), its energy-minima were established for a number of starting structures, which covered various mutual orientations of the guests and major conformations of the trimer's backbone. The resulting geometries could be roughly divided into two groups, *i.e.*, one maximizing the number of hydrogen bonds between DAT residues and the guests, and the other featuring a "hydrophobic pocket" in the mid part of the DAT trimer occupied by one of the guests and stabilized mostly by stacking. Representative structures were used to estimate their RI-MP2 interaction energies  $\Delta E$  extrapolated to the complete basis set limit by applying the variational supermolecular approach together with the cc-pVDZ and cc-pVTZ basis sets [3]. Interestingly, the stabilization of the hydrogen-bonded and stacked fragments was found to be similar for the most stable structures (*e.g.*, the  $\Delta E$  of the uracil-DAT pair in such arrangements was 87 and 78 kJ/mol, respectively). This finding could be instrumental for an interpretation of the experiments [1], [2].

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## P 97 - Tue

### ORIGIN AND ADEQUATE MODEL OF COALESCENCE IN QUIESCENT POLYMER BLENDS

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The growth of the size of dispersed particles in molten quiescent immiscible polymer blends is well documented. On the other hand, no explanation of this effect is commonly accepted. There are two mechanisms which cause coarsening of the phase structure: coalescence and Ostwald ripening. Evaluation of available experimental data led us to the conclusion that the rate of coalescence increases with interfacial tension. It qualitatively agrees with the theory of the molecular forces induced coalescence but it is in strong disagreement with theory of the Ostwald ripening [1]. This result clearly demonstrates that molecular forces induced coalescence is main mechanism of the particle growth in quiescent polymer blends. On the other hand, available theory of coalescence induced by molecular forces is approximate. It neglects mutual effect of molecular forces and Brownian motion on the rate of coalescence and it considers interaction of a droplet with its nearest neighbour only. Therefore, the theory cannot provide reliable dependences of the coalescence rate on the temperature and volume fraction of the dispersed phase. Moreover, the theory was derived for a system of spheres randomly distributed in space at the coalescence origin. In most polymer blends, dispersed droplets are anisometric at the end of mixing. It has several consequences which should be considered at interpretation of experimental results. The average distance between a droplet and its nearest neighbour is shorter for anisometric than for spherical droplets. The shape of anisometric droplets relaxes in quiescent state. Therefore, an anisometric droplet moves away of its neighbours in the direction of its major axes and approaches them in perpendicular directions.

Available results show that the growth of dispersed particles in quiescent immiscible polymer blends is caused by their coalescence induced by molecular forces and Brownian motion. Mutual effect of molecular forces and Brownian motion, many particle interaction and anisometric shape of the particles at the end of mixing should be considered at further studies.

#### **Acknowledgement**

The author is grateful to the Grant Agency of the Academy of Sciences of the Czech Republic for financial support (grant No. IAA200500903)

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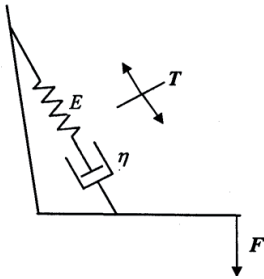
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### DIFFERENTIAL LAW FOR ENERGY TRANSFER IN MUSCLES

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There are many processes in which we feel that some energy is consumed (we are working) and the simple models say that we are doing nothing. A typical example of such a performance is carrying a heavy suitcase via a long horizontal road to the railway station. The problem is that even for holding the suitcase the muscles in the arm must be active. We must feed the muscles; the energy transfer to the muscles is necessary to prevent the fall of the suitcase. An analogical system and its rheological model are given in the attached figure. A luggage is held in horizontally positioned forearm. The weight of the luggage  $F$  and the weight of the forearm produce the tension force  $T$  acting on the Maxwell model which is used to model the rheological properties of the muscle system holding the forearm. If we



take the muscle system as a passive rheological element the deformation  $\epsilon$  of it, due to the model used, is

$$\epsilon = \frac{T}{SE} + \frac{Tt}{S\eta}.$$

$S$  is the cross section of the model,  $t$  is time,  $E$  the Young modulus and  $\eta$  the viscosity. The flow deformation  $T \cdot t/S\eta$  leads to energy loss (energy dissipation)

$$W = T\Delta l = \frac{Tl_0Tt}{S\eta}.$$

$\epsilon = \Delta l/l_0$  ( $l_0$  is the initial length of the model). If we instead of the whole energy loss use the loss in unit volume at unit time interval we obtain for the power  $p$  dissipated in unit volume the result

$$p = \frac{W}{Vt} = \frac{W}{Sl_0t} = \frac{T^2l_0t}{S^2\eta l_0t} = \frac{1}{\eta} \sigma^2.$$

The last equation is the differential law for power loss in unit volume. If we want to maintain the muscle in its position without relaxing, we must supply each unit volume of it by the power  $p$  given by the last equation. The viscosity term  $\eta$  is space dependent and says how much power is needed to maintain the stress  $\sigma$  in the given place. In soft parts of the muscle  $\eta$  is relatively small and energy transfer is large, in



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### **POLARONS IN POLYMERS, DETERMINATING ITS DYNAMICAL PROPERTIES**

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Polysilanes are potential materials for building molecular wires for future electronic devices based on one molecule. Their main-chain is composed of single bonded silicon atoms, which are sigma-conjugated. This feature cannot be seen in carbon backbone molecules, because their sigma orbitals do not extend far enough. Slowly moving charge carrier on soft molecule causes, that structure around it is deformed and phonon frequencies are shifted. These changes are moving along with the carrier and all-together they are called polaron. These changes will trap the charge carrier on the site thus estimation of the depth of potential well created around the charge carrier is the aim of this study.

In this work we studied poly[pheeryl(methyl)silylene] (PMPSi) by quantum chemical methods. We employed B3LYP method for optimalization of PMPSi molecules of different lengths. Then we calculated IR spectra for each different length of the molecule and estimated every compound of polaron binding energy. Resulting dependency allowed us to extrapolate binding energy for polymer length of about 20 monomer units, what is believed to be the maximum delocalization length of PMPSi.

## P 100 - Tue

### MODELING OF CHARGE CARRIER TRANSPORT IN CONJUGATED POLYMERS DOPED BY POLAR ADDITIVES

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A classical model of charge transport in disordered organic solids was developed by Bässler.<sup>1</sup> It is based on charge carrier hopping among sites (point approximation) which are distributed in energy. We have modified this model in order to extend the description for polymers, i.e., point sites have been substituted by rods (polymer chains). Thus, charge carrier transport involves both the on-chain motion through the conjugated system and hopping between adjacent chains. On-chain transfer integrals and site energies were randomized by the chain conformational disorder and by the electrostatic interaction of the charge carrier with dispersed polar additive. The charge carrier states are calculated using the tight-binding Hamiltonian. The inter-chain charge carrier hopping is modeled using the quasi-classical Marcus approach, taking into account the thermalization of the charge carrier between any subsequent jumps.

The obtained results show a very strong dependence of the charge carrier mobility on the dipole moment and concentration of the additive. If the additive dipole moment is doubled, the mobility may be reduced by several orders of magnitude. The calculated temperature dependence of the mobility shows essentially Arrhenius-type behavior with a moderate sub-Arrhenius deviation at the low additive concentration and the low-temperature saturation at the high additive concentration.

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## P 101 - Tue

### PROPERTIES OF COPOLYMERS ADSORBED ON HOMOGENOUS AND PATTERNED SURFACES

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Computer simulations of idealized models of polymer chains at interfaces were carried out by means of the Monte Carlo method. The models chains consisted of united atoms (beads) and were embedded to a [310] hybrid lattice. Each macromolecule was built of two kinds of beads: hydrophobic ( $H$ ) and hydrophilic ( $P$ ) ones and some sequences of beads were studied. The polymer beads interacted with a long-distance contact potential and were placed near an impenetrable and attractive surface. The properties of the model system were determined using the Replica Exchange Monte Carlo algorithm. The influence of the sequence, the temperature, the strength of the adsorption and the sequence of beads on the properties of chains were studied. It was shown that the most pronounced influence of the adsorbing surface on the chain's structure was observed for amphiphilic polymers ( $HP$ ) $_{N/2}$ .

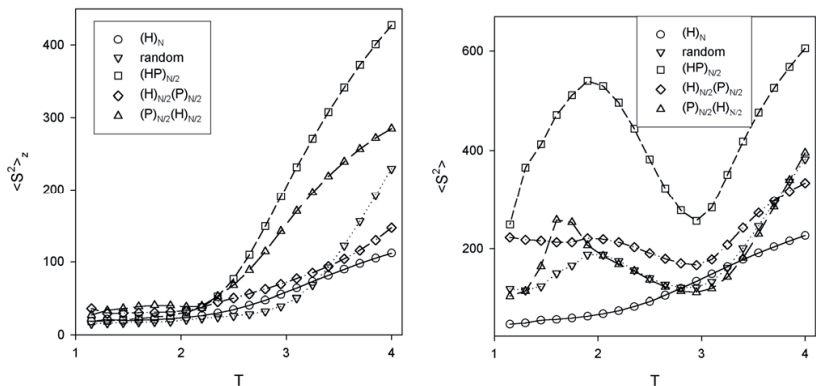


Fig. Changes of the chain's size as a function of the temperature for some sequences. The case of a weak adsorption (left) and a strong adsorption (right).

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# P 102 - Tue

## STRUCTURE OF THE MULTI-CHAIN POLYMER SYSTEM CONFINED IN AN ADSORBING SLIT - MONTE CARLO SIMULATION

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The aim of the study was the investigation of star-branched polymer molecules located between two parallel and impenetrable surfaces which were attractive for polymer segments. The chains were constructed of united atoms (segments) and were restricted to knots of a simple cubic lattice. Since the chains were in good solvent conditions the only interaction between the segments of the chains was the excluded volume. The properties of the model chains were determined by means of Monte Carlo simulations with a sampling algorithm based on chains' local changes of conformation. We found that at certain conditions the polymer chains were adsorbed at one of the confining surfaces, than after a certain period of time they detached from this surface and approached the opposite wall; this jumping was repeated many times. It was found that the mechanism of switching from one surface to another was an 'all-or-none' type. We observed that the adsorbed chains formed specific structures which were distinguished as trains, loops, tails and bridges (see Fig.1 for details). The analysis of those structures for different polymer segment densities and the size of the slit was discussed. It was found that the ability of forming the given structure depends strongly on both: the position of the bead in the chain and the segment density on the system as is shown in Fig.2.

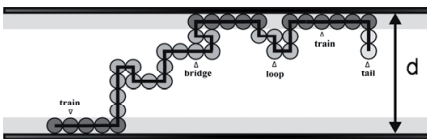


Fig.1 Scheme of the polymer in an adsorbing slit. The structures are shown with arrows.

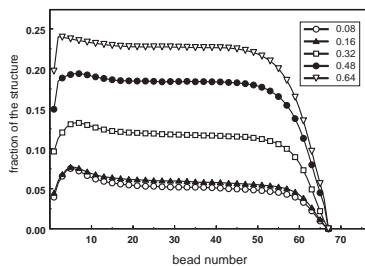


Fig.2 Fraction of bridges as a function of bead number for  $d=5$ . The segment density is given in the inset.

## COMPARISON OF PHYSICAL PROPERTIES AND MECHANICAL STABILITY OF ALGINATE HYDROGELS PREPARED BY INTERNAL GELLING DEPENDING ON THE ALGINATE TYPE AND GELLING CONDITIONS

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Alginates belong to the group of natural polysaccharides, which are products of marine brown algae. Polymer chain of alginate is composed of two monomers, the guluronic acid (G) and manuronic acid (M), which determine the properties of alginate hydrogels in terms of diffusion properties and chemical and mechanical stability. This contribution will deal with the alginate hydrogels made of Protanal LF 10/60 and Protanal LF 10/60 LS (both FMC BioPolymer) with high content of G and high content of M monomeric units, respectively. Chemical properties (swelling and syneresis), mechanical stability and optical properties of alginate hydrogels prepared from high G vs. high M alginates are compared.

Alginate gels were prepared in two successive steps. In the first step, the gel is formed by internal gelling method which is followed by diffusion gelling method.<sup>1</sup> Internal gelling, as step 1, is based on insoluble  $\text{CaCO}_3$  at  $\text{pH} > 7.5$ , which upon action of slowly hydrolyzing latent acid like GDL (D-glucono- $\delta$ -lactone) dissolves and releases  $\text{Ca}^{2+}$  producing alginate/ $\text{Ca}^{2+}$  gels.<sup>2</sup> The specific feature of internally gelled alginate hydrogels is that they are homogenous in terms of the spatial alginate distribution. A number of gelling buffers for step 2 can be proposed based on the information in the literature.<sup>2</sup> Typically they are also based on the ionotropic gelling using small cations ( $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ). It has been recommended to strengthen the hydrogel beads gelled only with  $\text{Ca}^{2+}$  by an addition of a small amount of  $\text{Ba}^{2+}$  ions to improve the stability under physiological conditions.

For determination of the effect of gelling conditions, the internally gelled alginate hydrogels were prepared of 1 wt.%, 2 wt.% and 4 wt.% Protanal LF10/60 and Protanal LF10/60 LS, respectively, using 30 mM  $\text{CaCO}_3$  and 30mM GDL. Prepared hydrogels were incubated in the gelling solution with various compositions in terms of  $\text{BaCl}_2$  and  $\text{CaCl}_2$ . Analysis of swelling and syneresis showed that internal gelling (step 1) results in a slight weight loss known as the syneresis for all hydrogels. After step 2, the syneresis as well as swelling was observed depending not only on the alginate type but also on gelling solution. It was observed that gels showed a similar trend for all studied concentrations in one gelling solution, but significant differences were observed among different gelling solutions. In this contribution we demonstrate that selection of gelling solution is a crucial step for obtaining hydrogel with required properties.

*This work was supported by the Sixth Framework Program of the EU, IP-031867, P. Cezanne and by the Slovak Research and Development Agency under the contract No APVV- 51-033205.*

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## P 104 - Tue

### SHAPE TRANSITION ON CONFINEMENT OF FLEXIBLE AND STIFF MACROMOLECULES

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Many biological macromolecules are characterized as stiff chains and macromolecular confinement is fundamental to many biological as well as technological processes. Properties of confined chains or chains in crowded environment, however, differ from macromolecules in free space. Moreover, our understanding of confinement effects is mostly based on flexible chains and there are still open problems in transfer of this knowledge to stiff macromolecules.

Our aim is to elucidate how the properties of confined macromolecules change by transition from flexible to stiff chains using simulations of discretized bead-spring wormlike chain model. We vary the chain stiffness from flexible chains to macromolecules representing the stiff genomic macromolecules and concentrate on the tubelike or spherical confinement of macromolecules with confinement radius  $D$ . While for flexible chain in channel there is only one basic regime in chain elongation curves  $R(D)$ , for stiff chains we estimate the ranges of two regimes of elongation for the strong and for the moderate confinements. The stiff macromolecules are found to be mostly ideal while the expected theoretical prediction based on confined excluded volume chains can be applied only for very long macromolecules. The range of covered confined chain lengths here is up to 2000 effective segments.

Further insight into the confined structures and hairpin formation in channel at certain persistence length  $P$  of chain and the extent of confinement  $D$  is provided by the results based on structure factor, the bond orientation correlation along the chain, the average persistence length and its distribution. For spherical confinement we investigate another structural transition, namely a confinement induced shape transition from disordered globule observed for flexible chains to the toroidal structure for stiff chains.

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# PC 105 - Tue

## THE INFLUENCE OF GOLD NANOPARTICLES ON ELECTRICAL CONDUCTIVITY OF POLYALKYTHIOPHENES

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We have investigated the electrical properties of the nanocomposites based on gold nanoparticles and  $\pi$ -conjugated polymers: poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT). Tetradodecylammonium bromide, TDAB, stabilized gold nanoparticles were prepared using two-phase synthesis based on the reduction of gold chloride trihydrate,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , by sodium borohydride,  $\text{NaBH}_4$ , with TDAB as a transfer agent. The composites were prepared by mixing the respective polymers (P3HT, P3OT) dissolved in toluene with nanoparticles dispersed in the same solvent. After filtration the solutions were precipitated in methanol to remove TDAB stabilizer and to replace it by the polymer. The content of nanoparticles in the polymer varied between 0.6 to 4.9 vol %.

The thin films of neat polymers and composites were prepared using spin coating technique. The electrical conductivity was measured on films cast on substrates equipped with interdigital gold electrodes. The presence of metallic nanoparticles increased the electrical conductivity of the composite but the concentration of gold nanoparticles was below the percolation threshold. The electrical conductivity of the composites was found to decrease exponentially with the interparticle distance. In neat polymers, the electrical conductivity raised with temperature up to 80 °C and 70 °C for P3HT and P3OT, respectively. The activation energy of electrical conductivity,  $E_a$ , was 0.16 and 0.28 eV as corresponds to the values reported in literature. After reaching the critical temperature the conductivity tends to decrease with further increasing temperature due to the morphological changes in the polymer. For the composites with Au nanoparticles, the turning point where the conductivity starts to decrease shifts toward 110°C and 100 °C for P3HT and P3OT, respectively. The activation energy of both types of the composites was about 0.3 eV, independently on the concentration of Au nanoparticles.

# PC 106 - Tue

## IN SITU OBSERVATION OF ACTIVITY OF HEMOGLOBIN AND CYTOCHROME *c* ON SOLID/LIQUID INTERFACES BY SLAB OPTICAL WAVEGUIDE SPECTROSCOPY

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Cytochrome *c* (cyt. *c*) and hemoglobin (Hb) have been probably most extensively studied by many researchers for understanding their functions. We have developed a novel technique using slab optical waveguide (SOWG) spectroscopy, with which absorption spectra in UV-vis region from adsorbed materials below a monolayer coverage were observed. Using indium-tin-oxide (ITO) electrode thin film on a SOWG (ITO-SOWG), in situ observation of molecules adsorbed on electrode surface can be performed under electrochemical condition. We have performed in situ observation of adsorption process, reactivity, and electron transfer reaction of cyt. *c* and Hb by SOWG spectroscopy and electrochemical techniques. In this presentation, I report these results and try to discuss the comparison of functions of these two protein molecules immobilized on solid/liquid interfaces.

The SOWG system was the same to that described previously.[1-3] A 150-W xenon lamp (System Instruments Co., Ltd., Japan) was used as the light source. The SOWG spectra were detected using a CCD detector with monochromator (PMA-11, Hamamatsu Photonics, Japan). A 50- $\mu$ m thick glass plate was used as a SOWG, and the thickness of ITO films were about 20 nm. The cell length was about 10 mm and the surface area of ITO-SOWG covered with sample solution was about 1.0 cm<sup>2</sup>. The guided light was propagated through the glycerol drop put on the SOWG surface. ITO-SOWG plates were cleaned by soaking in ethanol for 1 h and then rinsed extensively with Milli-Q water. In electrochemical measurements, the ITO electrode potential was controlled with a potentiostat (PAR Model 273A). The counter and reference electrodes were Pt wire and Ag/AgCl, respectively. Horse heart cytochrome *c* and hemoglobin were purchased from Sigma and used as received. The sample concentration of proteins were 5  $\mu$ mol/dm<sup>3</sup>, and the phosphate buffer was used as a solution (pH 7.2).

Absorption spectra of adsorption process of cytochrome *c* and hemoglobin on quartz and ITO electrodes were successfully obtained *in situ* using SOWG spectroscopy. Also the electron transfer reactions of surface immobilized proteins were investigated by in situ observation of absorption spectra by ITO-SOWG spectroscopy. Even after the adsorption on to the ITO electrode, cytochrome *c* and hemoglobin showed the electrochemical activity.

These results suggested that surface immobilized proteins showed activity without any further surface modification. It has been clearly shown that SOWG is a strong tool to understand the molecular activity on interfaces.

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## P 107 - Tue

### **SYNTHESIS OF PLA-MPEG AND PCL-MPEG DIBLOCK COPOLYMERS BY MICROWAVE HEATING**

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One of the most attractive advantages of microwave heating is its rapid bulk heating compared with the conventional method. Block copolymers of lactide or caprolactone with PEG can be synthesized by conventional heating by ring opening polymerization (ROP). However, this process is usually very time-consuming because it takes several hours to complete. Microwave heating allows us to prepare these block copolymers in extremely short reaction time. In this study, synthesis of diblock copolymers of caprolactone/lactide with polyethyleneglycol (PLA-mPEG and PCL-mPEG) by microwave irradiation was reported. For comparison, some of the copolymers were synthesized by conventional method (oil bath). Structural and functional characterization of diblock copolymers were performed by FTIR, <sup>1</sup>H-NMR and molecular weight values were determined by GPC and <sup>1</sup>H-NMR. Effects of microwave irradiation time and catalyst ratio were also investigated. According to the results, similar products were obtained both in oil bath and microwave synthesis. Average reaction time and catalyst ratio were estimated as 30 min and between 1-3 (mol%), respectively. Reaction times higher than 60 min caused low conversion and molecular weight values. Polymer conversions were not lower than that of in conventional heating. It was concluded that microwave heating substantially reduced the reaction time and resulted in formation of similar compound as in conventional method without any disadvantage.