

European Centre of Bio- and Nanotechnology

Technical University of Łódź

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**Workshop on Progress
in Bio- and Nanotechnology**

Abstracts

Łódź, Poland
12-14 February 2009

All contributions were submitted in camera-ready forms and are printed on the full responsibility of the authors

ORGANISED BY

Technical University of Łódź

and

BioTechMed Consortium

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The European Centre of Bio- and Nanotechnology (ECBNT) project is realized within the framework of the BioTechMed consortium formed by the academic institutions in Łódź.

An aim of the Workshop is to identify the most important issues and trends in bio- and nanotechnology in order to define future research profile of the Centre. The program will focus on three main research areas: Energy, Health and Environment, as recommended by the ECBNT's International Advisory Board (IAB) after its first meeting on 20-21.10.2008 in Łódź. Members of IAB have kindly accepted an invitation to give plenary lectures at the Workshop; the plenary sessions are followed by specialized sessions which demonstrate research potential of the ECBNT partners, with the special emphasis on the cooperation with leading scientific centers in Poland and abroad.

PROGRAMME

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Chairs: Z. Lisik, A. Napieralski, J. Ulański

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Saturday, February 14, 2009 Friday

9:00 – 11:00	Joint meeting of IAB and Scientific Council of ECBNT; discussion on the research profile of the European Centre of Bio- and Nanotechnology
Afternoon	Social program, departures

LECTURES

(in chronological order)

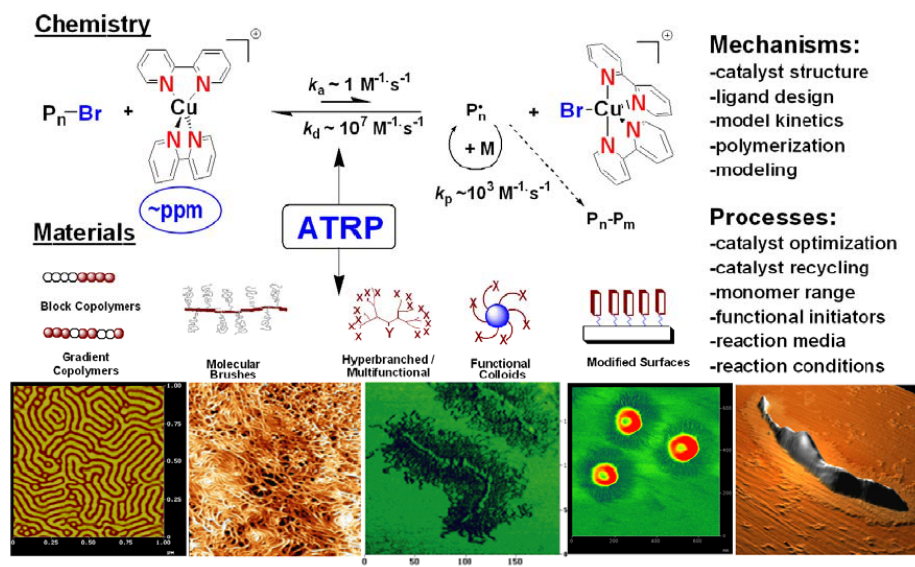
MACROMOLECULAR ENGINEERING FOR NANOSTRUCTURED MATERIALS

Krzysztof Matyjaszewski

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Macromolecular engineering is a powerful tool for preparation of targeted functional nanostructured materials [1]. It includes: (i) rational design of the macromolecular structure including chain size, uniformity/heterogeneity, topology, microstructure (sequencing and tacticity), composition and functionality; (ii) precise synthesis with high selectivity at reasonable cost, both in effort and environmental impact; (iii) assembly of macromolecules to supramolecular objects via controlled processing, including temperature, pressure, solvents, mechanical stresses, etc.; (iv) detailed characterization of the prepared materials at both molecular and macroscopic level. It can be also assisted by modeling of polymerization and processing conditions to aid in the design of appropriate conditions to reach targeted properties and function, and optimization of the entire process.

Scheme below presents some principles of ATRP (atom transfer radical polymerization) which is among the most efficient techniques for macromolecular engineering. It illustrates underlying and enabling synthetic chemistry procedure based on reversible atom transfer, it shows some examples of the molecular architectures available from ATRP and also some self-assembled or pre-assembled nanostructured materials [2]. The (co)polymers made by ATRP and other controlled radical polymerization processes have many potential applications as components of coatings, elastomers, adhesives, surfactants, dispersants, lubricants, additives, but also as specialty materials in biomedical and electronic areas and could affect the annual market of ~\$20 billion.



\$\$:NSF, DoE, EPA, DARPA, & ATRP/CRP Consortia: Akzo, Arkema, Asahi, Atofina, ATRP Solutions, Bayer, BFGoodrich, Boston Scientific, BYK, Cabot, Ciba, Ciba Vision, CIP, Dainippon Ink, Degussa, Dionex, DSM, Elf, Encapson, Evonik, GE, Geon, GIRSA, HTIG, JSR, Kaneka, Lion, Mitsubishi, Mitsui, Motorola, 3M, Nalco, Nippon Gosei, Nitto Denko, PPG, Rohm & Haas, Rohmax, Sasol, Solvay, Teijin, WEP & Zeon

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EXOPOLYSACCHARIDES FROM YEASTS AND (YEAST-LIKE) FUNGI

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Microbial Technology, Faculty of Bioscience Engineering, Ghent University, Belgium.
(Erick.Vandamme@UGent.be)

Several basidiomycetous and ascomycetous yeasts and fungi are known to produce (capsular) extracellular polysaccharides (EPS). Most of these EPS contain D-mannose, either alone or in combination with other sugars or phosphate. A large chemical and structural variability is found between yeast and fungal species and even among different strains. The types of polymers which are synthesized can be chemically characterized as mannans, glucans phosphomannans, galactomannans, glucomannans and glucuronoxylomannans. Despite these chemical differences, almost all of these fungal exopolysaccharides display some sort of biological activity, either malign or beneficial. The latter ones find already application in chemistry, pharmacy, cosmetics or as nutraceutical or probiotic. Furthermore, some yeast exopolysaccharides, such as pullulan, exhibit specific physicochemical and rheological properties, making them useful in a wide range of technical applications. Other fungal EPS, such as scleroglucan (produced by *Sclerotium gluconicum*.) find use in the oil industry, where it facilitates crude oil recovery, and as a matrix for drug delivery systems. Schizophyllan is produced by *Schizophyllum commune* and is in use as an immunostimulatory anti-malignant tumor agent. The biosynthesis, genetical and bioprocstechnological aspects related to fungal EPS formation have so far not been sufficiently studied, so as to allow for improved high yielding fermentation and recovery processes. First, a survey is given of the characteristics, the production and the application potential of currently well studied yeast and fungal extracellular polysaccharides. Own research data will then focus on the exopolysaccharides produced by *Tremella mesenterica* NRRL-Y-6158, named tremellan. It is composed of an α 1,3-D-mannan backbone, to which β 1,2-side chains are attached, consisting of D-xylose and D-glucuronic acid. Physicochemical fermentation parameters were optimised to produce high tremellan levels. Implementation of fed-batch and cyclic fed-batch fermentation with extra glucose feed increased the EPS-yield further to 10 g/l. The *Tremella*-polymer displays a pseudoplastic behaviour, but its viscosity is – surprisingly – drastically lowered by the presence of starch. It is thixotropic with a very fast recovery, a characteristic which is also delayed by starch. Tremellan displays some useful technical properties, such as thickening and high waterholding capacity as well as film forming ability, which might result in its use as a coating material for pharmaceutical and food applications. Tremellan was also shown to stimulate the immune system, using an *in vitro* neutrophil cell assay system.

These examples indicate the great potential of yeasts and fungi to produce a wide variety of exopolysaccharides. This is a domain of industrial biotechnology, where so far only the tip of the iceberg has been explored.

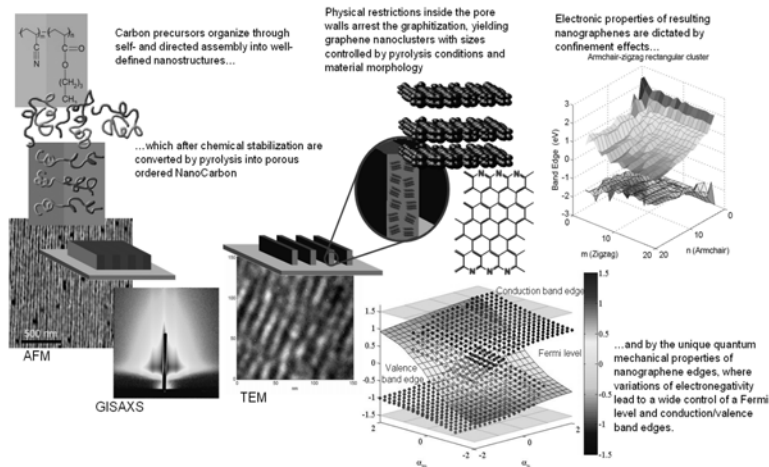
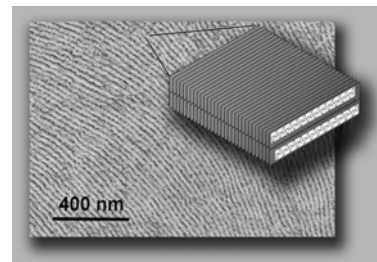
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CONTROL OF NANOSTRUCTURE IN π -ELECTRON MATERIALS: TOWARD CARBON-BASED NANOELECTRONICS

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This presentation will describe results of our recent work on two approaches utilizing macromolecular self-assembly as a route to novel nanostructured carbon π -electron materials. These approaches involve 1) control of nanostructure in homopolymers and block copolymers of regioregular poly(alkylthiophenes)^{1,2} and 2) synthesis of porous nanographenes through pyrolysis of self-assembled block copolymer precursors containing polyacrylonitrile^{3,4}. The first approach will be illustrated with AFM, TEM, electron- and x-ray diffraction results, demonstrating formation of various nanoscale morphologies (from granular to extended ribbons or "nanowires"), depending on solidification conditions and polymer composition. Proximal probe-based characterization of electrical properties of these nanostructures and their impact on performance of field effect transistors will be also discussed. The second approach will be illustrated by the examples of a variety of carbon nanostructures, ranging from nanodots, through nanofilaments to lamellae, prepared by thermal stabilization of nanoscale morphology and subsequent pyrolysis of block copolymers containing polyacrylonitrile and incompatible, sacrificial, block. The role of copolymer composition and processing conditions in determining the nanostructure, extent of graphitization, and optical and electrical properties will be described. Numerous potential applications of materials obtained by both approaches and their general promise for the field of carbon-based electronics will be discussed.



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OPTICAL TWEEZERS IN NANO-(BIO)-PHYSICS

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Optical Tweezers (OT) are experimental tools which are based on photonic forces acting on a micro- or nanoparticle. Its position in space can be determined with the precision of (± 1 nm) and forces acting on it are measured in the range between 1 - 100 pN with the extraordinary resolution of (± 50 fN). This enables novel experiments with *single* polymerchains and *isolated* colloids. In this review briefly the principle of OT will be explained and its impact for Nano-Bio-Physics will be exemplified with the following experiments: (i) Measurement of the force-separation dependence of *single* chains of double-stranded DNA having different length (ii) Forces of interaction between blank colloids in media of varying ionic strength (iii) Forces of interaction between DNA-grafted colloids in dependence on the grafting density and the molecular weight of the chains. (iv) Direct measurements of receptor/ligand interactions on a *single* contact level and (v) direct measurements of the electrophoretic mobility of single colloids.

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- [6] Otto, O.; C. Gutsche, F. Kremer, U. F. Keyser, "Optical tweezers with 2.5 kHz bandwidth video detection for single-colloid-electrophoresis", *Rev. Sci. Instr.* **79**, 023710 (2008)
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NANOSCALE PHENOMENA IN MODIFICATION OF POLYMERS: FROM CARBON BLACK TO ION BOMBARDMENT

Otmar Dobrowolski and Dariusz Bieliński

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The presentation discusses the results of several scientific projects from the area of the materials engineering of polymer-based composites containing inorganic nanoparticles.

Additionally, activities concerning surface engineering of polymer nanocomposites, including chemical modification of the surface of polymers as well as physical modification are presented.

The detailed outline of the presentation includes:

- influence of morphology, in the meaning of filler particles dispersion and distribution on physical properties of polymer / filler composites,
- fabrication of nanocomposites containing carbon nanotubes,
- application of silver nanoparticles to polymer in bulk as well as immobilization on its surface,
- modification of polymer based dental composites,
- tribochemical modification accompanying friction of polymer – metal couple,
- ageing and chemical modification of the surface layer of polymers, and
- physical modification of the surface layer of polymers using ion bombardment.

CONTROLLED PHOTO-SYNTHESIS OF GOLD NANOPARTICLES

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The deep interest in preparation and investigations of metal nanoparticles has beginning since 1970's, because of their potential applications in different fields like physics, chemistry, optoelectronic, biology, medicine, and interdisciplinary fields.

We present a study of the photochemical method for the synthesis of gold nanoparticles. Metal nanoparticles were obtained in an aqueous medium with pH values ranging from 6,5 to 8,0. The system include hydrogen tetrachloroaurate(II) HAuCl_4 , triethanolamine used as an electron donor, hexadecyltrimethylammonium bromide and tin(IV) porphyrin which played role as a photosensitizer.

The particle growth process was monitored by ultraviolet-visible spectroscopy. Time-dependent UV-VIS spectra show one or two plasmonic bands, in the visible range, which correspond to the formation of nanoparticles with different morphology.

The morphology of the particles was evaluated by Transmission Electron Microscopy (TEM) and Tapping mode Atomic Force Microscopy (AFM).

APPLICATION OF TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY TO THE SURFACE STUDIES OF SELECTED SOLID MATERIALS

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Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a very useful technique for surface studies of different types of solids. It allows a simultaneous recording of all emitted ions in a wide mass range (up to 10 000 amu), and achieving high transmission of secondary ions, high sensitivity and high mass resolution. Moreover, owing to the use of secondary ion mass spectrometers with time-of-flight analyser the information from the top monolayers of the investigated surface (not only on the elemental but also molecular level) can be obtained. An application of ToF-SIMS usually does not demand employing a special procedure of sample preparation. On the other hand the main disadvantage of time-of-flight secondary ion mass spectrometry is related to the “matrix effect”, which hinders performing qualitative measurements [1].

The literature data [2,3] concerning the use of ToF-SIMS to the studies of solids is very extensive and indicates that this technique can be applied to the investigations of biomaterials, biomolecules, drug delivery systems, polymers, materials used in electronic industry, different organic surfaces (i.e. self-assembled monolayer surfaces), environmental samples, organic coatings, surface contaminations, catalysts, minerals, paper, glass, etc. The main goal of this work is to demonstrate the applications of time-of-flight secondary ion mass spectrometry to the surface studies of above mentioned groups of solid materials on the basis of both the measurements performed in the Institute of General and Ecological Chemistry at Technical University of Łódź and literature data.

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SOL-GEL CHEMISTRY IN NANOTECHNOLOGICAL APPLICATIONS

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One of the most versatile techniques commonly used in nanomaterials' engineering and nanotechnological applications is sol-gel chemistry. It offers broad possibility of preparation of many metal oxides, composites, organic-inorganic hybrids and other materials in the form of mesoscopic objects (fibers, nanorodes, nanoparticles) as well as thin structured films, porous materials and nanocomposites.

In this work the illustration of these possibilities is presented. Silica nanorodes prepared with the use of various templates is shown as an example of the synthesis of elongated ceramic materials. Another part of this study is devoted to the preparation of titania nanoparticles, which are considered as promising material in such applications as solar energy conversion, photocatalysis, biomedical systems etc.

Next, the preparation of nonporous or porous titania and zirconia ultrathin layers deposited in sol-gel dip-coating procedure is described. The material morphology including porosity level and pore-size was controlled by application of appropriate type and concentration of surfactants or polymer beads which served as template. These types of materials may be applied as sensors, catalysts, low- k materials, photonic crystals etc.

Furthermore, the synthesis of nanocomposite systems based on titania or alumina layers containing hard ceramic nanoparticles (Al_2O_3 , ZrO_2) is presented. Application of nanoparticles considerably enhances the mechanical and tribological properties of the material.

Atomic Force Microscopy (AFM) was used in all experiments of surface and nanoobjects imaging.

NANOPARTICLES METROLOGY USING ATOMIC FORCE MICROSCOPY

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Nanotechnology demands nanoparticle characterization, e.g., size, shape, and mechanical properties, due to the potential role of nanoparticles in a variety of applications. Atomic force microscopy (AFM) has been identified as a major tool for imaging and size measurements of nanoparticles in spite of the challenges they pose due to strong surface forces: Nanoparticles have to be strongly connected to the surface to overcome the competing probe-particle interaction. If not, the imaging attempts result in unintended removal or displacement of particles.

A capability of AFM that has not been adequately explored is to measure the mechanical properties through a force-distance (probe sample separation) (f-d) analysis (Fig.1). In this mode an AFM probe is brought down onto the particles and the force response is measured as a function of probe displacement. A careful analysis of these measurements can give insights into the nanomechanical properties of individual nanoparticles.

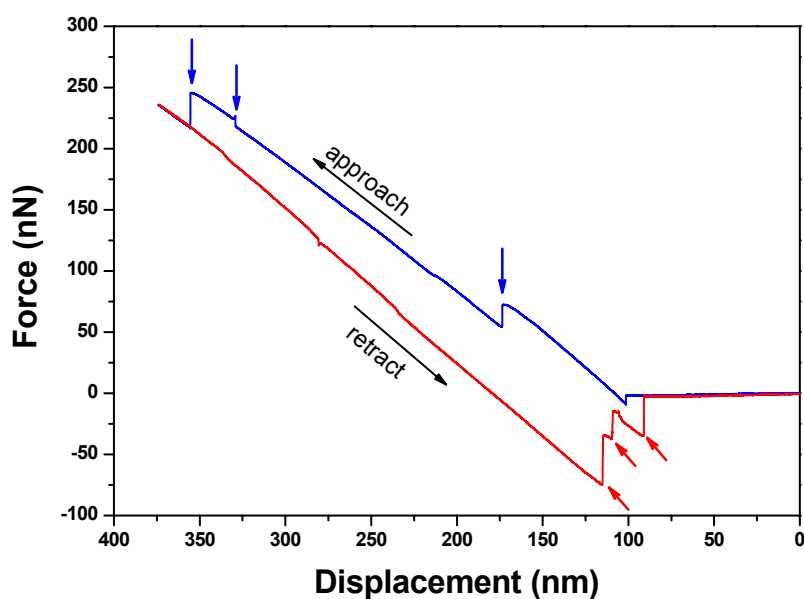


FIG. 1 Typical force-displacement curve of nanoparticles aggregates.

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MODIFICATIONS OF GOLD NANOPARTICLES FOR BIOMEDICAL APPLICATION

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Keywords: gold nanoparticles, AFM, DLS, nanoparticles modifications

Modified gold nanoparticles (AuNP) are nanomaterials with an area of application that grows quickly. On the AuNP surface a wide spectrum of chemical and biochemical compounds may be attached with following functionality: fluorescent markers, antibodies, therapeutic drugs, NMR contrasts, isotopic labels and others. Successful application of this kind of modifications depends on size and stability of AuNP. Presented work is focused on the synthesis and characterization of AuNP. First step of the modification was performed by reaction of cystamine with the AuNP surface. After this reaction amine functional group is present on the AuNP surface and plays a double role for future incorporation of bioactive compounds. First of all $-NH_2$ group plays a role of anchoring point for a variety of compounds which have no opportunity to react with gold surface directly and secondarily it helps to stabilize gold colloidal solution. To control size and stability of colloids the following analytical methods were used:

- AFM and SEM microscopy for imaging, size and size distribution measurement of nanoparticles
- DLS with Zeta potential measurements for characterization of colloid stability in pH 1,8-14 range.

As a final result of presenting work we obtained

Well-characterized monodisperse AuNP of the size range from 10 nm to 60 nm modified by cystamine were obtained. Colloids are prepared for final modification by bioactive molecules.

This work was supported by MNiSW Grant No: N N507 350435

OPTICAL PROPERTIES OF SILICON NANOCRYSTALS IN SILICA

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Silica matrix containing silicon nanocrystals (Si-nc) is a photonic material with a large variety of promising applications [1]. In this contribution, we present a series of experimental data on optical characterization of this material. The experiments were performed on thermally annealed silicon-rich silicon oxide films and Si/SiO₂ superlattices prepared as substrate-supported and free-standing layers. Raman spectroscopy characterizes Si-nc in silica matrix, and the 1.5-eV photoluminescence (PL) is strong in these samples. A spectral filtering of PL observed in these systems allows measuring their optical properties [2,3]. In particular, evidence of birefringence is provided with these experiments and supported by m-line measurements [4]. The extracted optical properties are in agreement with chemical composition estimated by X-ray photoelectron spectroscopy [5]. The red-NIR PL of these samples shows systematic correlations with the optical and structural properties. Based on this, the PL mechanisms are discussed [6].

The work was supported by the Academy of Finland through the Finnish Center of Excellence “Computational Molecular Science” and the FinNano Project “Optical and Surface Properties of Nanoparticles”. Cooperation with Sergei Novikov, Timur Nikitin, Olli Kilpelä, Jouko Lahtinen, Rama Velagapudi, Markku Räsänen, Juha Sinkkonen, Claudio Oton, Daniel Navarro-Urrios, and Lorenzo Pavesi is gratefully acknowledged.

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NANOSCALE DIAMOND MATERIALS: A PLATFORM FOR BIOMEDICAL ARENA

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Nano- and bio-technological advancements put forward the needs for new materials and approaches for tissue engineering, thus supporting innovative strategies, by which new combinations of biocompatible, yet inert material can be employed together with living cells or bioactive proteins in order to sustain regeneration and repair of damaged, diseased and aged tissues. For this purpose, following the pyrolytic graphite application in artificial heart valves novel carbon materials such as carbon nanotubes, fullerenes [1], hard amorphous carbon films [2], nanocrystalline diamond (NCD) films [3] and diamond particles [4] have been applied.

Pertinent biomaterial requirements are biocompatibility, chemical stability, and mechanical strength which are perfectly fulfilled by NCD coated surfaces [5]. However, while diamond nanoparticles usually exhibit reach surface chemistry right after the synthesis and purification, NCD films do not. This requires often non-conventional approaches to the surface modification of NCD to attain desired functionality, e.g., the usage of plasma termination that provides either enhanced cell attachment (H-terminated) or can completely block it (F-terminated) as shown in Figure 1. However, the methods to control chemical or biological modifications of diamond surfaces have not yet been well established.

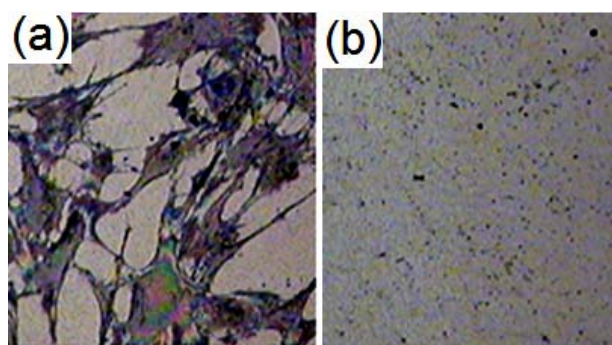


Figure 1. MSCs attachment to (a) Hydrogen- and (b) Fluorine-terminated NCD.

This presentation provides further an overview of properties and recent progress in surface engineering and modification of NCD thin films and diamond nanoparticles, and the functionalization of these materials for creating a stable platform for highly selective cellular response, bio-labeling, therapeutics, and for integration of

microelectronics with biological modification and sensing.

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MICROWAVE PLASMA FOR CNTs DEPOSIT CONTINUOUS FABRICATION AT ATMOSPHERIC PRESSURE

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Carbon nanotubes (CNTs) deposit on various substrates is urgently required for many technological applications such as electron emitters, supercapacitors, rechargeable batteries, photovoltaic cells, drug carriers etc. Of all the various CNTs so far discovered, the production of multiwall CNTs was identified as the best candidate for scale-up and industrialization. One of the main challenges to obtain the optimal product properties is the dispersion in matrix. This requires carbon radicals and metal catalyst atoms uniform aerosol concentration to be treated in some time by the adequate temperature around 1000°C.

Among all the methods of synthesis for CNTs the Chemical Vapor Deposition (CVD) of liquid aerosols hydrocarbon/metallocene is one of the most efficient and flexible provided that metal catalyst is gasified and heated up to the reaction temperature. We have being using pure plasma synthesis methods and PACVD with different setups of hybridization (Fig.1).



Fig.1 Arc plasma CNT synthesis – left and Microwave-CVD hybrid CNT synthesis - right

Plasma Assisted CVD process allows the synthesis of clean multi walled CNTs with low content of sub-products such as metallic particles and amorphous carbon. The velocity of growth can reach high values such as 50 m/min and the length can be varied from some tenths of microns to few parameters according to synthesis parameters. The process control requires on-line FTIR spectroscopy. Currently we have been trying deposition on solid substrates represented by quartz or silicon but our work is targeted to use soft substrates as well.

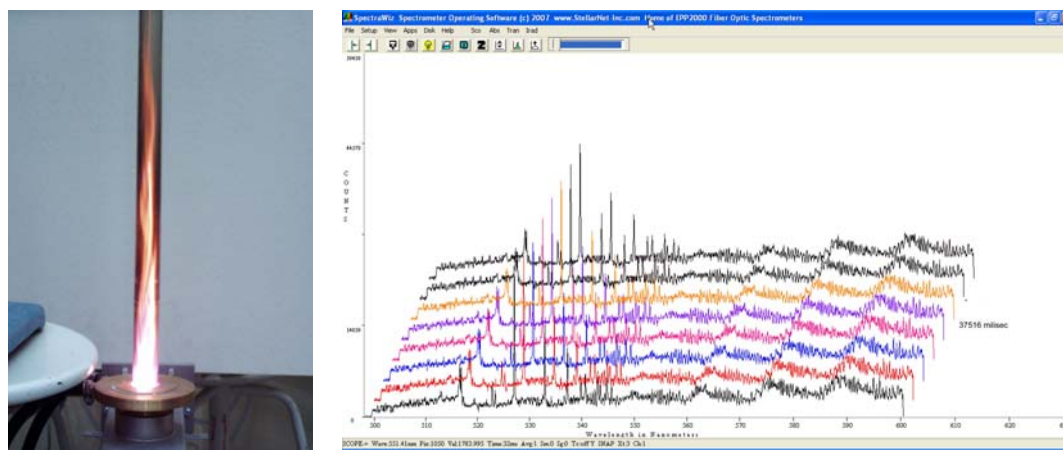


Fig.2 Microwave enhanced plasma jet carrying deposit material - left and plasma spectrum- right

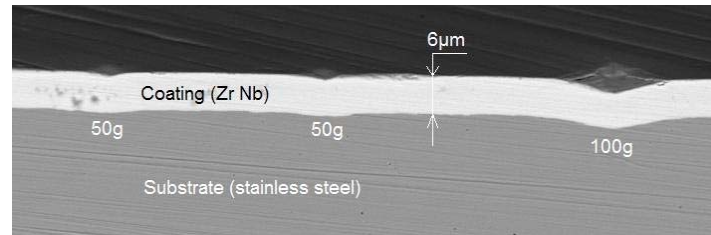
PROCEDURE FOR PVD COATINGS HARDNESS MEASUREMENTS BY MEAN OF A MICROHARDNESS TESTER

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Most of the time, hardness of PVD coatings is measured by nano-indentation. This technique needs some material which is not really wide spread for the moment. This work presents – as an alternative to nano-indentation – a new method for measuring coatings' hardness by mean of a microdurometer with low loads and a Sweeping Electronic Microscope. This kind of apparatus is less sensitive to some parameters as : surface's roughness, indent's defects, superficial passive or oxide layers, external disturbances as vibrations,...This work takes into account all the requirements which are necessary for hardness measurements under good conditions. For example, in case of an indentation's depth higher than 10% of the coating, the result is highly influenced by the substrate. The procedure which is presented here allow to become free of the substrate and the load's influence (phenomenon known as Ident Size Effect). Results which are presented deal with 3 to 6 μ m coatings of Zirconium-Niobium nitrides deposited on stainless steel substrates but the technique can be applied to different coatings.

Keywords

Micro-hardness, coatings, SEM, Zirconium, Niobium, Nitriding.

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DIAMOND MICROFLUIDIC DEVICES

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The selection of optimal material and optimal manufacturing technologies is a key issue in designing a new generation microfluidic device [Karczemska 2002]. Diamond's extreme properties such as the highest known thermal conductivity, remarkable bio-adhesion properties, high electrical resistivity and chemical inertness, make it a great material for this application [Björkman 2001].

In the present work we focus on manufacturing a diamond microfluidic device for quick separations of DNA and proteins by electrophoresis. A transfer moulding technique, a sort of net-shape technique, will be used to grow the diamond microfluidic devices structures on sacrificed substrates [Ralchenko2004]. This approach is based on diamond deposition from gas phase on pre-patterned templates to produce exact copy of the pattern after removal of the substrate.

The experimental work has been done already, and examples of open channels in CVD diamond have been demonstrated.

Acknowledgement

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[2]

NANOMATERIALS FOR AUTOMOTIVE INDUSTRY

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The research of nanolayers and functional nanostructures in thin coatings will be purpose-oriented on the improvement of usable properties of important materials, e.g. the development of self-cleaning and super hard layers and products usable for the protection of the environment. The preparation of methods for the optimising of usable mechanical, electrical, magnetic, optical and other properties of composite and nanostructural materials and their dependency on the preparation and on the parameters of nanofibres and nanoparticles, which make up these materials.

The efficient transfer of knowledge, which would widen the spectrum of industrially useful technologies based on the practical utilisation of nanolayers, nanostructures and nanocomposites in the materials manufacturing. The assessment of possible impacts on the industrial production and environment [1,2].

Acknowledgement:

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NANODIAMOND POWDER PARTICLES FOR MEDICINE

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Unusually advantageous features of diamond, first of all good biocompatibility and high hardness are accompanied by its poor properties – mainly brittleness which eliminates this material from the majority of medical applications. Applications to steel medical implants is not possible through a direct combination of a covalently bonded material, such as diamond, with a materials characterized by metallic bonds. A result of our studies, was a development of a deposition method of a nanocrystalline diamond film, adhesively bound, through a carbide interlayer, with the metallic substrate [1]. A concept of the gradient transition from carbide forming metal to diamond film was applied. The studies of carbon films as coatings for implants in surgery were aimed at the investigations of biological resistance of implants, histopathological investigations on laboratory animals, tests of corrosion resistance, measurements of mechanical properties and a breakdown test in Tyrode's solution. Finally: carbon, especially in the form of the nanocrystalline diamond film, have found industrial applications in the area of medical implants. Different medical implants are covered by Nanocrystalline Diamond Coatings. NCD forms the diffusion barrier between implant and human environment.

The additional aim of the study was to confirm a high degree of diamond compatibility with the human organism in order to investigate the so called extended surface. For this reason, the diamond powder particles was a subject of investigations. A novel assay for testing the biocompatibility of highly dispersed solid-state biomaterials was developed and applied to DPP preparation [2].

Physical and chemical carbon nanoparticles properties present unlimited potentials for biological and medical applications. Most of the *in vitro* studies indicate nanodiamond biocompatibility as a carbon related material [2]. Therefore, the recent study presents significant effect of nanodiamonds on redox homeostasis (SOD, GPx, and GR). Based on SOD activation and concomitant GPx deactivation, we demonstrate diamond nanoparticles prooxidative activity within red blood cells. Our study did not confirm systemic oxidative stress caused by nanodiamonds administration, while the concentration of blood plasma TBARS and TAS remained unaffected. The demonstrated results indicate the emerging demand for further extensive studies regarding to establishment of minimal toxic doses of nanodiamond as well as detailed estimation of biological properties of detonation diamond nanoparticles in studies *in vivo*.

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MICRO- AND NANO-DIAMONDS FROM EXTRATERRESTRIAL MATTER

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The presence of diamonds in meteorites was confirmed for the first time in the Novo-Urei ureilite in 1888. Mainly diamonds occur in three types of meteorites : chondrites, especially in carbonaceous chondrites; ureilites and iron meteorites (Canyon Diablo) [1].

First mentioned type carbonaceous chondrites contain up to 3500 ppm of diamonds this type is called presolar diamonds – nanodiamonds because they are older than Solar System. Diamonds have usually 2 – 3 nm size (up to 10 nm), their origin is still discussed (Supernovae) but process could be low-pressure condensation similar to CVD. Diamond from ureilites have quite different origin (HPHT) and size (μm). They are set in carbon vein like area between olivines minerals. Diamonds from Ureilites was create on Ureilitic Parent Body during impact process. Last type of diamonds are discover in Canyon Diablo iron meteorite, and this is typical (HPHT) origin during impact to the Earth.

Our investigation of diamond from meteorites, are based by Micro – Raman spectroscopy. Diamond peak was discover in carbonaceous chondrite Allende 1326 cm^{-1} [2] and in ureilites. In this second group be obtain diamond peaks from 1321 cm^{-1} to 1334 cm^{-1} , such differences of Raman shift can be caused by few things including size of crystal, polytypes of diamond or shock process [3]. Statistic research of diamonds in ureilites show different types of diamond in various sample in the same meteorite type [4]. Diamonds in extraterrestrial matter is a good indicator of process on space and meteoritic Parent Bodies.

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AMORPHOUS POLYMER COMPOSITES WITH NANOFILLERS : INFLUENCE OF THE NANOPARTICLES ON THEIR MOLECULAR DYNAMICS

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In many applications additives in polymers are fillers like montmorillonite, silica, carbon black or zinc oxide or cross-linking agents, dispersants and anti-degradants, used in order to improve their properties such as processing, tensile strength, wear resistance and performance.... Filler particles are mostly composed of the primary particles but can be strongly bonded to other primary particles to form aggregates and agglomerates. In the case of the montmorillonite basal distance relates to the intercalated dispersion state.

In this work we discuss the influence of nanofillers on the molecular dynamics of organic-inorganic hybrid materials by means of DSC, DMA and BDS.

Two types of amorphous polymer matrix are under study, varying the process and the amount of the incorporated nanofillers. First a PETg matrix was chosen because it is unable to crystallize (copolymer of terephthalic acid, ethylene glycol and 1,4-cyclohexane dimethanol) which is mixed with Montmorillonite (MMT) chosen as a modifier with an important specific surface. Also a carboxylated acrylonitrile-butadiene rubber matrix is filled in situ by the sol-gel process [1-5] using N-2-aminoethyl-3-aminopropyltrimethoxysilane. Furthermore, the amino groups on the alkyl substituent of the silane has to act also as cross-linking moieties.

The nature and the dispersion mode of the nanofillers in the systems under studies influence on the relaxation phenomenon of the composites. In the first example PETg-montmorillonite we have shown that the incorporation of MMT leads to decrease the amount of vitreous phase able to relax at the glass transition, accelerates the kinetics of relaxation of this vitreous phase, makes stronger the liquid glass former and does not modify the β - relaxation characterized using the apparent activation energy E_a . So, this is the cooperative behaviour of the vitreous phase that is drastically modified by a small amount of MMT.

In the second example, it was of interest to determine the mobility of the elastomeric systems as the subsequent hydrolysis and condensation reactions of methoxy groups provided the silica filler with better dispersion when compared to the composites containing the silica added during the preparation of rubber mixes. Also the dynamic analysis demonstrates that these composites are crosslinked with ionic bonds, created by the interactions of amino groups of the silane and carboxyl groups. Structural relaxation behaviours relate quite well to the molecular dynamics of the composites under studies.

GLASS TRANSITION DYNAMICS IN CONFINED AND LOW-DIMENSIONAL SYSTEMS: FROM NANOPOROUS GUEST/HOST SYSTEMS, SMECTIC LIQUID CRYSTALS TO ULTRA-THIN POLYMER FILMS.

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The nature of the glass transition remains one of the most interesting unsolved problems in the physics of condensed matter. One key idea towards a deeper understanding of the glass transition is the assumption of a *correlation length* ξ for the dynamics in glass forming liquids, which increases in size as the temperature is lowered. The study of spatially confined glass forming systems is, therefore, an attractive way to determine ξ .

The aim of the lecture is to present experimental evidence for *finite size effects*, i.e. confinement induced deviations in the glass transition dynamics, using dielectric relaxation spectroscopy (DRS), calorimetric and pyroelectric techniques. Results are discussed from various *small molecule* glass forming systems [1-3] and *ultra-thin polymer films* [4-8], which represent systems of different *dimensionality* and *molecular order* of the glass forming ensemble. Despite the structural diversity, typical cooperativity lengths in the order of $2 < \xi < 5$ nm were found for both polymeric and low molecular mass systems.

Finally, a novel, alternative approach to determine ξ is proposed, which relies on the *variation in the confinement length* under real-time conditions. This idea was implemented recently by DRS measurements on ultrathin layers of glycerol, sorbitol and threitol during organic molecular beam deposition (OMBD).

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POLYMER BASED NANOCOMPOSITES - INTERPLAY BETWEEN INTERFACIAL AND BULK EFFECTS

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Polymer based nanocomposites continue to receive tremendous attention for different applications. They show remarkable property improvements (increased tensile properties, decreased gas permeability, decreased solvent uptake, increased thermal stability and flame retardance) when compared to conventionally – scaled composites. Different polymer based nanocomposites are prepared where polypropylene, polyethylene, polycarbonate and polystyrene are used as polymer matrices. As nanoparticles montmorillonite (CLAY) [1], layered double hydroxides (LDH) [2], multiwalled carbon nanotubes and polyhedral oligomeric silsesquioxanes (POSS) [3,4] are used. The property – structure relationships of these nanocomposites are investigated by dielectric spectroscopy and gas transport measurements (permeation, sorption). Additionally FTIR, DSC and density measurements are applied. The results are discussed with regard to the phase structure of the nanocomposites. Especial attention is paid to characterize the interfacial region between the polymeric matrix and the different nanoparticles. This regards also to estimate the length scale of interaction between the nanoparticle and the matrix.

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MOLECULAR DYNAMICS IN INTERCALATED POLY (PROPYLENE-OXIDE) AMINES / LAYERED SILICATE NANOCOMPOSITES

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Polymer-layered silicate nanocomposites (PLSN) have attracted much attention because of significant improvement in several properties in comparison to pristine polymers. For the synthesis of PLSNs the choice of layered materials is often the smectite clays (e.g. montmorillonite, hectorite) due to their highly expansive characteristic and their rich intercalation chemistry which allows them to be chemically modified and to become compatible with the polymer precursors. It is well established that macroscopic properties in PLSNs depend on the choice of the clay mineral and the type of organic modifier that greatly affect interfacial interactions and nanoscale morphology of the polymer - layered silicate. Recently, a new method of preparing epoxy-clay nanocomposites has been proposed [1]: the direct incorporation of poly (propylene oxide) amines (also used as epoxy curing agents) in the galleries of montmorillonite clays via ion-exchange.

The aim of this work is the investigation of the molecular dynamics of poly (propylene oxide) amines intercalated in montmorillonite clays by means of Differential Scanning Calorimetry (DSC), Thermally Stimulated Depolarization Currents (TSDC) and broadband Dielectric Relaxation Spectroscopy (DRS) methods. The amines of interest were the commercially available α , ω -diamines known as Jeffamine D-series amines with molecular weights in the range 400 – 4000. Poly (propylene oxide) amines exhibit the dielectric normal mode due to the fluctuation of the end-to-end vector as well as the segmental mode due to local, segmental fluctuations. Dielectric Spectroscopy, thus, can provide information on the chain dynamics monitoring all the possible motions of the macromolecules, from local chain motions up to global chain translational and rotational motions.

Our results reveal a remarkable dependence of the long range molecular mobility of the intercalated diamines (with both chain ends attached to the silicate surface) on the chain length of the polymeric chains and on the basal spacing of the organoclays. Specifically, for the intercalated D400 (the shortest chain, ~ 6 repeating units) the segmental relaxation is strongly suppressed whereas for the intercalated D2000 and D4000 the segmental mobility is retarded (the effect being less pronounced for the longest chains). Varying gallery height (i.e. the available space for chain motion) and tuning the level of interaction among diamines' head groups and the negatively charged surface of the clay platelets we are able to investigate the effects of restricted geometry on the molecular dynamics in our PLSN system. The results are discussed in terms of chain configurations, polymeric chain - clay surface interactions and confinement effects.

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MOLECULAR DYNAMICS IN MACROMOLECULES WITH DIFFERENT ARCHITECTURE

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The molecular dynamics in polymers depends strongly not only on chemical structure of macromolecules but also on their architecture and supramolecular structure. In last decade there were realized in Department of Molecular Physics of Technical University of Lodz several international projects, which goal was beside others, the investigation of molecular dynamics of different polymer systems.

Perfluoropolyethers (PFPEs) are the family of medium-low MW polymers composed entirely of carbon, fluorine and oxygen atoms, which exhibit liquid phase behaviour over very wide temperature range (-100°C to 450°C). The PFPE materials have generally very low dielectric constant, which depends strongly on the chemical structure of these materials. The incorporation of the hydrogen atoms or hydroxyl group instead of fluorine in the end groups is enough to increasing the dielectric constant few times. Also the molecular relaxation strongly depends on molar mass. The differences in the glass transition in this family are even tens degrees.

Another project has concerned of polyurethanes (PU). Their properties strongly depend on their chemistry and resulting architecture. The main goal of this work was the investigation of molecular dynamic of the polyurethanes with different architecture, linear and hyperbranched, and of their blends with different compositions. The DSC measurements showed that the linear PU has two glass transition phenomena and that the hyperbranched PU has only one. Relaxation phenomena investigations allowed to describe the miscibility of these two PUs. The PU networks

The block copolymer samples with variation of the composition gradients within the blocks constitute interesting examples of possibilities to modify the structure and properties in broad range. Two specific cases were considered in this work: (1) the nearly symmetric AB diblock copolymer consisting of a pure butylacrylate block A and a block B with a composition gradient of butylacrylate and methylmethacrylate comonomers; and (2) the symmetric triblock BAB. In all samples a microphase separated state is observed by means of DSC and SAXS. Main effect related to replacing pure methylmethacrylate block by blocks with composition gradients with increasing contents of butylacrylate consists in a decrease of the glass transition temperature of the mixed microphase whereas the glass transition of the block A remains nearly constant. Results indicate possibilities of a wide variation of properties by means of small changes of composition distributions of comonomers in the two types of gradient copolymers.

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THE MOLECULAR DYNAMICS IN SUB-ZERO TEMPERATURES IN PVME HYDROGELS

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Hydrogels prepared of poly (vinyl methyl ether) (PVME) are of special interest of pharmacy and medicine industries as they exhibit a volume-phase-transition at ca. 37°C [1]. Solutions of PVME as well as gels reveal however, the most complex and still not fully understood, properties in sub-zero temperature range [2-4], where dynamics of liquid water, ice and polymer strongly influence each other [5]. These peculiar properties are much more interesting in hydrogels, in which PVME constitutes 3-dimensional permanent network.

In this work molecular relaxation in series of radiationally crosslinked PVME hydrogels were investigated by broadband dielectric spectroscopy (BDS) in the temperature range -100 ÷ 0°C. Variations in temperature dependence of observed relaxation processes were correlated with changes in water-polymer and water-water interactions studied by Raman spectroscopy in temperature range -173 ÷ 0°C. Finally, the amount of uncrystallised water fraction in studied hydrogels were determined from dielectric, Raman and calorimetric (DSC) measurements. Such comparison allowed us to draw some general conclusions on the species of bound water which differ in their vibronic states, mobility in an electric field or freezing/melting ability.

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THERMODYNAMIC PROPERTIES OF POLYMER CHAINS. THE COMPARISON OF SOME MONTE CARLO TECHNIQUES

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In last decades, a rapid development of simulation methods applied to study the properties of polymer and biopolymer systems has been observed. However, for the most macromolecular systems, models were rather complicated and contained enormous amount of parameters and, therefore, it is sometimes difficult to judge which of them are really important in order to obtain proper results. This was the main reason for designing and studying simple models of biopolymers. A coarse-grained model of polymer chains was thus designed and studied [1]. In our model we replaced a real macromolecule with a sequence of statistical segments (united atoms) while the remaining atomic details were suppressed. Such a chain was restricted to a lattice of a [310] type which was frequently used in simulations of polymers and biopolymers (the bond fluctuation model). Two kinds of polymer beads were defined: hydrophilic and hydrophobic (HP model). They were arranged in some sequences. The force field used consisted of the long-range contact potential between residues and the local potential preferring some conformational states. In order to obtain the thermodynamic description of our model we used the Multihistogram (WHAM) method (the procedure that relies on a mutual overlap of the probability of states in the neighboring replicas) combined with the Parallel Tempering (the Replica Exchange) Monte Carlo sampling scheme [2]. Optimal set of temperatures for the Parallel Tempering simulations was found by an iterative procedure. The simulations using the Wang-Landau algorithm (Multicanonical Monte Carlo method) were also carried. The influence of the temperature and the force field on the properties of coil-to-globule transition was studied by the above mentioned methods. It was shown that the WHAM and Wang-Landau methods could give more precise results when compared to a Metropolis and Replica Exchange methods.

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DYNAMIC LATTICE LIQUID MODEL AS A TOOL TO INVESTIGATION OF NON-EQUILIBRIUM PROCESSES

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Computer simulation has become one of the major tool in material science, which provides an insight in molecular structures and dynamic behavior under various specific conditions. There are many algorithms for the simulation of simple as well as complex systems (polymer solution, reaction front, fractal growth etc...) on a lattice, but only few of them can work with density factor $\rho=1$ (such statements indicates that each lattice site is occupied by one molecular unit) and which properly reflect the dynamics over a broad time range. The Dynamic Lattice Liquid (DLL) model can work with density factor $\rho=1$ and became a basis for the first parallel algorithm which takes into account coincidences of elementary molecular movements resulting in local cooperative transformation.

We present applications of DLL model to investigate a simple non-equilibrium processes like reaction diffusion front problem [1,2] and non-equilibrium fractal growth [3].

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SPECIAL PURPOSE PARALLEL SUPERCOMPUTER BASED ON THE DYNAMIC LATTICE LIQUID MODEL

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Computer modeling is nowadays one of the most important sources of information about details concerning behavior of complex molecular and macromolecular systems at the molecular or atomic scale. Recently, very effective methods of atomistic, molecular or macromolecular modelling have been developed (Pakula and co-authors), named the Cooperative Motion Algorithm (CMA) and Dynamic Lattice Liquid (DLL) model [1,4] which allows for dynamic simulations in dense systems of complex molecules or macromolecules by considering natural possibilities of cooperative molecular rearrangements.

The main aim of this work is the construction of a dedicated computer (realizing the DLL architecture) with enormous computation power. The success of the discussed simulation methods has been demonstrated in numerous applications in which dense packing, specific interaction, complex molecular structures and complex hierarchical dynamics have important effects on behavior of modelled systems [1]. The already tested or potential applications concern all fields of science and technology in which atomistic, molecular, macromolecular and supramolecular structural and dynamic consideration are of importance or of interest.

Using the technique based on field programmable gate arrays (FPGA), a prototype machine was realized [2]. This machine is shown in Fig 6. It is hardware realization of DLL algorithm. The prototype contains 216 elementary DLL cells. It is composed of 7 PCBs (printed circuit boards). Six of them contains three XC3S4000 FPGAs on each board. In each FPGA an 2x6 array of DLL cells is implemented. Three FPGAs on the board constitute two dimensional array containing 36 (6x6) DLL cells. The seventh board, containing two FPGAs, controls the simulation being performed by six board constituting three dimensional array containing 216 (6x6x6) DLL cells. The execution of virtually unbounded simulations requires an implementation of cyclic boundary conditions. Therefore the construction of the machine is based on the cylinder shape in order to reduce the delay differences.

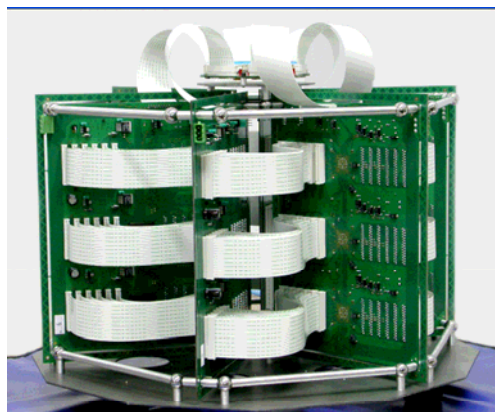


Fig. 1 view of the prototype.

Obviously, the developed model is useless as far as the realistic physical or chemical simulations are concerned. In practical applications the DLL array should have about 10^6 (100x100x100) elements. Anyway, the existing model allows for verification of the ideas and proposed algorithmic solutions.

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NANO- AND MICRO-SCALE ELECTRO-OPTIC MOLECULAR SWITCH BASED ON PHOTOCHEMICALLY MODIFIED MOBILITIES OF CHARGE CARRIERS - DESIGN vs. REALITY

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A dominant trend in design of electronic and photonic devices in recent decades has been a decrease of their dimensions. In molecular systems, it is in principle possible to design electronic devices based on premises deduced from properties of individual molecules. Among materials of interest, multistable molecular systems have attracted much attention. On the nano-scale, the multistable systems can act as elements of molecular switches. On the other hand, such systems can also be functional on the mezo- or macro-scale.

Photochromic molecules, capable of undergoing photochemically driven reversible reactions, are examples of bistable molecular systems. The simplest way of monitoring the photochromic reactions consists in measurements of optical spectra; in some devices, however, a direct electrical response would be more desirable. In these cases, photochromic molecules should be employed whose electrical properties would be modified in a controlled way by incident light. The switches described in the literature (see, e.g., [1-4]) consisted of photochromic moieties ('switches') incorporated in the main chains of π -conjugated polymers ('molecular wires'). We adopted a different approach: the switch has been attached to a σ -conjugated polymer as a side group or even has only been molecularly dispersed in the polymer [5-8]. Both the literature reports and our results confirm a possibility of effective switching. The architecture of such devices must, however, be optimized as presently used materials are rather slow. Moreover, there are additional requirements associated with relations between energy levels of the wires and the switches.

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CHARGE CARRIER RECOMBINATION IN ELECTROPHOSPHORESCENCE POLYMER COMPOSITES AS INVESTIGATED BY SPECTRALLY RESOLVED THERMOLUMINESCENCE

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Organic electrophosphorescence light-emitting diodes (OLEDs) using phosphorescence dyes emitting from their triplet states are intensively studied because of their high emission efficiency. The phosphorescent molecules allow harvesting light not only from the singlet but also from the triplet excitons; therefore, much higher than 25 % internal quantum efficiency can be achieved theoretically. High efficient OLEDs have been indeed reported by doping red to blue emissive iridium complexes in both a low molecular weight and polymer organic hosts. However, polymer light-emitting diodes (PLEDs) have attracted considerable interest due to easy processability in solution, which allows the application of spin-coating and printing methods for preparation of large- area and flexible display devices [1].

In this study, iridium complexes were used as the dopants, and poly(*N*-vinylcarbazole) (PVK) or mixture of PVK with derivative of oxadiazole (PVK/PBD) were used as the matrices. The charge trapping and radiative recombination are two essential processes influencing the efficiency of the electroluminescent devices. One of the most direct methods of investigation of the charge carriers trapping, detrapping and radiative recombination is thermoluminescence (TL) [2]. Moreover, using of spectrally resolved TL allows to distinguish a different types of excited states, traps and recombination centres which can be presented in the electroluminescent composites.

From comparison of the TL results for PVK and for PVK + 40 wt % PBD one can notice that TL maximum around 135 K is shifted by 20 K to lower temperature and main band of emitted light is red-shifted by 20 nm. The results indicate that origin of the TL maximum in PVK/PBD blend can be related to triplet (maximum at 550 nm) and singlet (maximum at 430 nm) exciplex formed between carbazole group and PBD molecule. The introduction of any type of the investigated iridium complexes to PVK and PVK/PBD results in disappearing of the monomeric emission in both high- and low-temperature peaks in TL. However each of the investigated dyes results in different changes of the TL spectrum in comparison to the neat matrices.

Generally, upon doping population of deeper traps considerably increases. Moreover it was noticed that the spectra of light emitted during the TL experiment correspond to the electroluminescence spectra. This means that the TL experiments reflect dominant recombination process occurring in electroluminescence phenomenon.

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MONOCLONAL ANTIBODY PURIFICATION: AN EUROPEAN RESEARCH INITIATIVE

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Recent developments in fermentation technology have strengthened the need to significantly improve the down-stream processing of biopharmaceuticals, since this is often considered as the bottleneck in the production process. The European Integrated Project AIMs (Advanced Interactive Materials by Design) is approaching this problem by integrating material and process development to optimise the performance of down-stream processing on the example of monoclonal antibody purification.

Nowadays, cost-intensive chromatographic affinity steps are often used to capture the target molecules and considered as a key element for the optimisation of the overall process. Within AIMs, the concept of affinity materials consisting of a support structure and specifically design ligands has been expanded to membrane chromatography and extraction to include the potential of other technologies.

New ligands are developed on the basis combinatorial chemistry and immobilised on improved supports. Molecular modelling results validated by X-ray crystallography give insight in the interaction of support, ligand, and target molecules to improve the understanding. The structure and performance of new materials for chromatography, membrane chromatography and extraction is characterised experimentally and advanced modelling strategies are used to develop simulation tools that allow correlating these properties. Different aspects of down-stream-processing are brought together to a generic approach for optimised process design in terms of productivity, yield, media consumption and investment in a short period of time. Mini-plant experiments complete the overall project approach and ensure the reliability of the theoretical work.

The AIMs project is funded within the 6th framework program (contract-No. NMP3-CT2004-500160) and comprises 24 partners from 12 European countries including 4 industrial companies, 4 SMEs, 14 academic institutions and 2 stakeholders.

CATALYTICALLY ACTIVE *N*-LIPIDATED PEPTIDES IMMOBILIZED ON SOLID SUPPORT

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We designed and prepared supramolecular structures formed by *N*-lipidated oligopeptides immobilized in the regular pattern on the cellulose surface which are able to specific binding of ligand molecule. Due to the conformational flexibility of the fragments forming the supramolecular structure, the shape and properties of the binding cavities are adjusted the most effectively to requirements of the guest molecules. The previous studies documented that process of binding guest molecules is highly selective, reversible and competitive. Therefore, we supposed that under favorable circumstances the structures could operate as catalysts if suitable, catalytically active molecular fragment are included inside the binding pocket. In order to verify this hypothesis we prepared library of supramolecular hosts with catalytic triade: His Asp(Glu) Ser, incorporated into the binding pocket (Fig. 1).

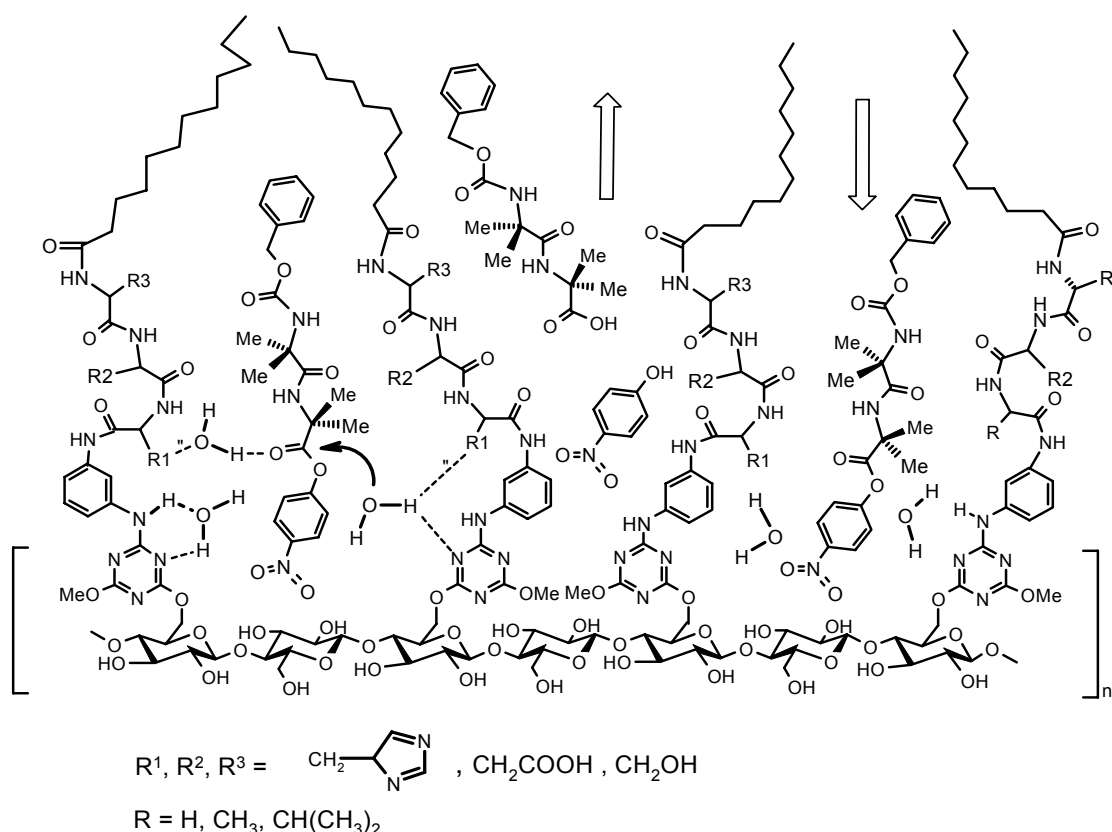


Fig. 1. Proposed mechanism of catalytic activity of *N*-lipidated peptides

For the first generation library the rate of hydrolysis of *p*-nitrophenyl esters of *N*-protected amino acids was measured by spectrophotometric determination of liberated *p*-nitrophenole in buffered, aqueous methanol and compared with appropriate data obtained in the absence of catalytic structures. The most active catalyst were selected from the library and their stability, selectivity and ability for re-use was studied. For the second generation of library the stereoselectivity of artificial esterase was studied. It has been found that enzymes prepared from natural L-amino acids hydrolyzed *p*-nitrophenyl esters of L-dipeptides, but D-enantiomers were resistant towards degradation.

GENETIC PROPERTIES OF *GLUCONACETOBACTER XYLINUS* E25 STRAIN

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In natural environments biofilms are microbial lifestyles. Microorganisms can survive in adverse conditions by dint of extracellular biofilm synthesis. Bacterial cellulose (BC), a polysaccharide produced by some of *Proteobacteria*, is a very interesting material with a great biotechnologic and biomedical potential. It displays many unique properties with comparison to plant cellulose such as higher purity, higher crystallinity, higher water absorption and stronger biological adaptability.

Gluconacetobacter xylinus is the most prolific bacterium of the cellulose producing microbes. Although this species is a common producer of BC, its productivity and aerobic requirements vary a lot between strains. The *G. xylinus* E25 strain is deposited at pure culture collection of Technical University of Lodz and is routinely used for cellulose dressings biosynthesis in stationary culture. On the other hand, in agitated cultures this strain exhibit unstable production by appearance of cellulose non-producing forms (Cel⁻) [1]. On contrary *G. xylinus* strain NQ5 (ATCC53582), is able to synthesize high level of BC, even in agitated cultures. Therefore we have started research on genomic differences between these two strains (NQ5 & E25). As genome sequence of the *G. xylinus* is unknown yet, for the initial studies SSH (*select subtractive hybridization*) technique was used.

Second attempt is to identify genes which are differentially expressed in these two strains. It is more probable that dissimilar productivity of compared strains is a result of various gene expression regulation, manifested on the level of transcripts or proteins. The next experiments will be carried on the post-transcriptional level (mRNA) using SSH method as well.

This investigations can be useful in further research, concerning the genetic aspects of cellulose biosynthesis and mechanisms of regulation of this process. Identified differences between the strains will bring some information about reasons of cellulose deficiency in *G. xylinus* cells. In future plans there is construction of modified E25 strain with more preferable characteristics from technological point of view.

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BACTERIAL CELLULOSE IN MEDICINE

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In stationary culture bacteria *Gluconacetobacter xylinus* E₂₅ produce a thick, slippery cellulosic pellicle at the surface of culture medium. The membrane is produced extracellularly and contains bacterial cells embedded inside. It is known that under suitable conditions as much as 50% of the supplied substrate carbon is assimilated into cellulose to produce the membrane of a highly reticulated, crystalline and ultra fine structure of nano-fibers.

Physicochemical properties, susceptibility to vascularisation and tissue overgrowing make this material perfect for medical applications. The high mechanical strength in the wet state, the substantial permeability for liquids and gases and low level of skin irritation render the gelatinous cellulosic membrane applicable as an artificial skin for temporary wound covering.

Latest studies showed that bio-cellulose, as a natural polymer produced by bacteria, is a highly biocompatible material. It has already found an application as a wound dressing but there are also experiments concerning its internal use as vessel substitutes and hernia meshes. Following specific modification process there is a possibility to produce cartilage-like substitute for trachea, auricular and nasal concha or even tubes for nerves regeneration. Obtained biomaterials are similar to natural tissues, with biocompatibility, mouldability, biophysical and chemical properties fitting the needs of plastic and reconstructive surgery. Some of these biotechnological products have been already applied in medicine, some others have been subjected to intensive clinical investigation.

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EXTREMOPHILES AS A SOURCE OF VALUABLE ENZYMES AND ACTIVE COMPOUNDS

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The term “Extremophiles” relates to various microorganisms that are capable of living and proliferating in extremely unfriendly environmental conditions like: high or low temperature, salinity, γ -radiation, high pressure, low or high pH value, low water content or presence of heavy metal ions.

Because of their unique survival strategies they are potential source of valuable biocatalysts and metabolites for medicine, environmental protection, pharmacy, chemistry, food industry, cosmetology and entertainment.

The Institute of Technical Biochemistry possesses collection of more than 150 cold-adapted (psychrophilic) microbial strains isolated from soil and marine water samples picked up in the neighbourhood of Henryk Arctowski Polish Antarctic Station (62°09'41"S; 58°28'10"W).

During over 15 years studies several enzymes, with great application potential, like proteases, lipases, β -galactosidases, esterases have been isolated, characterized and used for reactions carried out in bench-scale. Selected results of these studies will be presented.

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BIOSENSORS – WHERE WE ARE - WHERE WE GO

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Activity of the biosensor group in Institute of general Food Chemistry is presented. The group is concerned mainly on construction of biosensors with electrochemical and optical detection system. Amperometric biosensors were constructed on basis of oxygen electrode with oxidases immobilized in silica gel by sol-method [1,2]. The method of immobilization was optimised (gel precursor, composition, pH) to obtain enzyme electrodes with high sensitivity and applied to different oxidases and bienzymatic systems. The sol-gel method was also applied to immobilize enzymes on potentiometric tungsten electrodes [3]. It was found that tyrosinase electrode shows the potentiometric response to mono- and ortodiphenols with very low detection limit. It was proposed that the potential changes reflect the red-ox state of the enzyme. The sol gel-method was applied in fluorescence optode for glucose with pyrene as indicator [4,5]. Practical application of enzyme electrodes was tested in project QUALI_JUICE (CN 012461, VI Framework) concerned on use of lactate biosensors in fruit juice production .Because the main method of enzyme immobilization was the sol-gel method studies on sol-transition, state of fluorescent oxygen indicators and stability of glucose oxidase in silica gels were carried out [6-10].

New approach in sensor construction is mimicking of biological material by molecularly imprinted polymers. Functional fluorescent polymer with new fluorescent probe (styril pirydinum derivative) was synthesized and characterized for cAMP assay [11,12]. Molecular imprinting technique was also applied in order to produce polymeric material selective towards β -carboline alkaloids. Various experimental and computational methods were used to study the physicochemical properties of prepolymer and polymeric matrix and interactions with target molecule [13]. Another biomimetic approach is to use catalyst with catalytic function of the enzyme. This was done by inclusion of Cu^{2+} ions in silica gel with amine groups [14]. The obtained material can be used in amperometric and potentiometric electrodes showing the same activity as tyrosinase ones.

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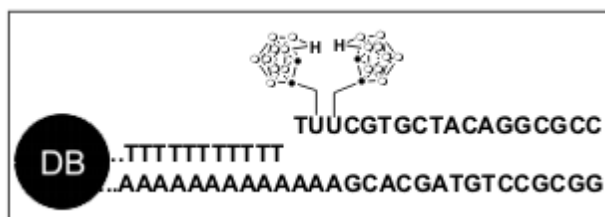
BIOSENSORS AND DNA CHIPS. EMERGING APPLICATIONS OF BORON CLUSTERS IN NANOTECHNOLOGY

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DNA chip technology is rapidly advancing and applications to diagnostics, gene discovery, gene expression and mapping have been convincingly demonstrated. Array-based assays allow a range of characteristics, such as drug resistance to be rapidly and simultaneously determined. Near instantaneous detection of pathogens from clinical material, combined with simultaneous prediction of their antimicrobial resistance profiles, would revolutionize the impact of microbiology on the management of infections [1].

Recent activity has focused on the development of hybridization assays based on various optical coding systems and allowing simultaneous detection of multiple DNA targets. Electrochemical detection of nucleic acids is an attractive alternative to established fluorescence and other optical coding technologies, with advantages including cost, sensitivity and direct electronic readout, and it is becoming frequently used in biosensors and DNA chips development [2,3].



Due to their unique structure and properties boron clusters find various applications in research and practice including emerging use in developing boron based nanostructured materials and devices [4,5]. The electrochemical activity of simple boron compounds has been known for a long time. With the discovery

of boron clusters in the 1960's the electrochemical properties of caged boranes, carboranes and their complexes with metals, metallaboranes and metallocarboranes have been the subject of extensive studies. Recently we proposed a new, original approach to the electrochemical DNA detection based on polyhedral boron clusters [6] and designed a prototype biosensor in which new indicator of DNA hybridization connected with commercial paramagnetic beads (DB) and a carbon paste electrode was utilized [7]. This and other recent findings on applications of boron clusters in design of new nanomaterials will be discussed.

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ANTI-AMYLOID APPROACHES BASED ON INHIBITORY NUCLEIC ACIDS

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Our recent studies have been focused on development of anti-amyloid approaches for prevention and treatment of Alzheimer's disease (AD), based on sequence specific silencing of genes involved in pathogenesis of this neurological disorder. According to the amyloid cascade hypothesis, accumulation of beta-amyloid peptides (A β) is the primary factor driving to neural degeneration. A β is the product of the proteolytic cleavage of the APP (amyloid precursor protein) substrate protein by beta- and gamma-secretases. It was demonstrated that beta-secretase (aspartyl protease Asp2), also called beta-site APP cleaving enzyme (BACE1), is an excellent target for anti-amyloid therapeutic drug design [1]. Till now, several approaches have been evaluated to find an effective inhibitor for human beta-secretase, mostly in the field of peptidomimetic, non-cleavable substrate analogues.

Our approach is based on targeting the BACE mRNA and its down-regulation with small inhibitory nucleic acids (siNAs) [2]. Those include catalytic nucleic acids (ribozymes and deoxyribozymes) as well as siRNAs. Plasmid-coded hammerhead ribozymes and synthetic deoxyribozymes 10-23 were the first found to be efficient inhibitors of BACE1 gene expression in a sequence-specific manner, measured, both, at the mRNA and protein levels [3,4]. Synthetic siRNA, as well as vector-coded shRNAs, proved to be able to down-regulate BACE1 mRNA in human cell lines as well as in adult mice hippocampal neural stem cells and animal model [5,6]. While silencing of BACE1 protein is shown to be safe for the cells and organisms, silencing of gamma-secretase by down-regulation of expression of its enzymatic component - presenilin 1 (PS-1) is lethal. The preliminary results on the allele-specific silencing of mutant PS-1 (L382V, C→G transition), which is the main cause of an early onset Familial Alzheimer's Disease (FAD). will be presented [6].

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SELF-ORGANIZATION OF PEPTIDES

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Molecular self-assembly offers unique directions for the fabrication of novel supramolecular structures and advanced materials. The inspiration for the development of such structures is often derived from self-assembling modules in biology, as natural systems form complex structures from relatively simple building blocks. Peptide-based nanostructures indicate an important route toward the production of ordered nanostructures as several studies had demonstrated their ability to form well organized assemblies. This includes cyclic peptides designed with alternating D- and L- amino acids, amphiphile peptides, peptide-conjugates and ionic self-complementary peptides.

An example of naturally occurring self-assembly process affording nano scale objects by polypeptides is amyloid fibril formation. These 7-10 nm fibrillar assemblies were already used for the formation of conductive nanowires. Also the short peptides have been used as model systems to study the molecular mechanism that leads to amyloid fibril formation. Based on the analysis of short amyloid forming fragments, it has been postulated that aromatic interactions may play a significant role in the self-assembling process. This hypothesis led to the discovery what is the core recognition motif of the Alzheimer's β -amyloid polypeptide (wild-type A β 42 DAEFRHDSGYEVHHQKLVF19FAEDVGSNKG AIIGLMVGGV and the variant with Pro19) [1]. The accumulation of aromatic residues has been also confirmed in the analogos sequence – amylin (IAPP - *Islet Amyloid Polypeptide*) which is a 37-residue peptide hormone secreted by pancreatic β -cells at the same time as insulin [2]. Amylin fibrils commonly found in pancreatic islets of patients suffering diabetes mellitus type 2, or harboring an insulinoma, can induce apoptotic cell-death in insulin-producing beta cells, an effect that may be relevant to the development of type 2 diabetes. This observation strongly stimulated search for understanding molecular information and mechanism needed to self assemble this novel class of peptide into nanotubes. The simplest objects prone to self-assembly are aromatic dipeptide, the diphenylalanine element and the diphenylglycine, forming nanotubes or spherical nanometric assemblies. Remarkably flexibilities of peptides fragments in formation of nanostructures recently has been considered important for many applications in various fields including molecular electronics, tissue engineering, and material science.

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CRYSTAL STRUCTURES OF Fc IN COMPLEXES WITH PEPTIDOMIMETIC LIGANDS

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Monoclonal antibodies (MAb) [1], due to their high selectivity to the target-specific receptors, are recently used as main anticancer drug components, as well as being utilized in many diagnostic tests. Their production is very expensive because of high costs of purification process. The current methods of MAb purification are based on chromatography columns with protein A or G agarose, which interact with the Fc fragment of the monoclonal antibodies. Proteins A and G are universal for use with a wide range of antibodies, however, they are expensive and impractical for purification on an industrial scale. Our research is a part of the European AIMs Project, the goal of which is to develop innovative, interactive materials, which could optimize cost-effective processes of MAb purification.

As a source of Fc for our studies we used an anticancer drug - Herceptin [2], in which the monoclonal antibody IgG1 is the active component. We performed the cleavage of IgG1 using papain to obtain an isolated Fc fragment, which after purification, concentration and buffer exchange was crystallized with ligands. Crystals were measured on the EMBL synchrotron in Hamburg. We determined a number of crystal structures of the Fc complexes with peptidomimic ligands. All structures were solved in the $P2_12_12_1$ space group. In the asymmetric unit, there are 2 monomers (A, B) creating a homodimer, the shape of which is reminiscent of a twisted horseshoe. The interactions of chains A and B in the crystal lattice are not identical. Chain A is involved in more crystal contacts and chain B has a better access to the water channels. The unit cell contains four homodimers related by three perpendicular two-fold screw axes. The domains of each monomer (CH2, CH3) possess predominantly β architecture. The CH2 domains are naturally glycosylated and a proper distance between them is maintained through the polysaccharide chains interactions.

The structural informations of the Fc-ligand complexes were used in the designing of a new generation of active components for chromatographic columns. In this research we used a method of ligand searching adapted from the current trends in drug design. The knowledge of structural interactions allowed designing more specific ligands, leading to better chromatographic material for protein purification, which will significantly reduce the overall costs of monoclonal antibody production.

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FERMENTATION ACTIVITY OF IMMOBILIZED YEAST CELLS

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Cell adhesion is the fundamental phenomenon that governs and describes bioengineering processes that employ microorganisms immobilization with focusing on different biotechnological applications, including beer and biofuel production. Immobilisation of cells has become popular in industrial processes due to the obvious advantages. Brewing industry is especially deeply interested for economical reasons, in brewery yeast cells immobilization and its application to continuous processes with increasing productivity of cells loading in bioreactors and the advantage of the reducing time of fermentation and maturation.

The leading idea of this study was to investigate cells growth, metabolic activity and fermentation ability of selected yeast strains, entrapped inside multichamber cores formed from foamed alginate or adhered on the surface of porous ceramic supports made from hydroxyapatite or chamotte.

The alginate multichamber beads were covered with an additional layer of 0, 1 % poly-L-lysine and 0,1M silicate gel to increase their mechanical stability and avoid the cells leakage. Percolated nanostructured ceramics fabricated from hydroxylapatite with a porous structure and opportunity to deposit the electrical charge on the surface and chamotte made from clay were used. Effect of adhesion and their stability, biomass growth and cell viability, evaluation of fermentation performance, ATP, trehalose and glycogen, carbohydrates and flavor and aroma profiles were examined. For these purposes new analytical methods were developed included gas and liquid chromatography, enzymatic assay of specific enzymes activities of cells in situ, and specific metabolites by HPLC and GC method. Biotechnological studies of main fermentation processes with the use of immobilized brewery yeast were conducted on laboratory scale using semi-continuous or yeast „repitching” method.

The results of the research with immobilized yeast have shown high ethanol production, proper profiles of green beer flavour, acceptable product quality, good yeast adaptation to conditions of fermentation process and the reduction of time required for primary fermentation from 10 to few days. Immobilized cells are considered to be more tolerant against ethanol than free cells. The extensive production of acetaldehyde in the green beer with immobilized cell does not present any technological difficulties. Yeast immobilization offers significantly shorter fermentation times, cheap carrier materials, reduction of investment costs and production of beer with generally acceptable and sufficiently balanced flavour, which levels can be controlled by manipulating the content of wort concentration, pitching rate, yeast strain and fermentation temperature. The course of primary fermentation process with immobilized yeasts was comparable to that with free yeast.

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MOLECULARLY IMPRINTED POLYMERS AS SMART SENSING ELEMENTS

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Molecular imprinting of polymers (MIPs), provides a powerful approach for obtaining effectively working sensory systems. Molecular imprinting is realized by copolymerisation of functional monomers in the presence of a target molecule that acts as a molecular template [1]. Subsequent removal of the template result in functionalised molecular cavities that are able to recognize the template molecule. The size and shape of the molecular cavity inside of the polymer and also the distribution of the functional groups forming the internal electronic structure of the cavity make that is able to selectively adsorb of the template molecule. The important element of the molecular cavity is a receptor. Interactions between the template and the receptor create changes of the electronic structure which are then transduce outside of the material as an electrical and/or optical signal.

We developed the MIPs as polymeric optical sensor in which one of the functional monomers is fluorescent [2]. The fluorescence measurements: steady-state and time resolved have been applied as analytical methods [3]. Recently we adopted the pyrazolequinoline derivative (highly fluorescent dye) for obtaining of the fluorescent MIPs that the fluorescence of the polymer is strongly changeable dependently on the analyte binding. The MIPs were polymerised as porous materials in bulk as well as thin-layer films.

For identification of peptides and bigger biological objects like microorganisms a surface molecular imprinting of polymers (SMIPs) methodology have been developed. The SMIPs technology leads to surface imprinted cavities with molecular memory of particular system-template. During the preparation process, the template by means of biological object like microorganism forms complex supramolecular structure with the functional monomers. After removing of the microorganisms the polymeric surface showing enhance of adhesion of the microorganisms to the imprinted polymer matrix [4].

The processing and monitoring of polymeric sensory systems for nucleotides with optically active receptors incorporated into the polymer will be discussed. The recognition and selectivity of adsorption of the template microorganism as well as identification of the *Saccharomyces cerevisiae* yeast cells using the surface imprinted polymer matrix also will be discussed.

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BACK TO THE FUTURE OF INDUSTRIAL BIOTECHNOLOGY

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The sustainable use of limited resources by nature to provide target molecules with biocatalytic reactions continues to be a role model for chemical synthesis. The application of biocatalysts to functional group transformations is shaped by the search for selectivity, the shift from fossil-based to biobased raw materials and the economy of molecular transformations like atom economy and step economy. Safety, health and environment issues are key drivers for process improvements in chemical industry and the development of reactions or pathways replacing hazardous reagents is a major factor determining the sequence of molecular transformations from raw material to product.

Biocatalyst production technologies and integrated process engineering have been instrumental in the establishment of biocatalytic reaction steps in chemical synthesis. The inherent properties of biocatalysts make them the privileged catalysts for highly selective asymmetric molecular transformations like e.g. hydrolysis reactions, oxidation reactions, carbon-carbon bond formation reactions as well as molecular unit transfer reactions. The universe of six enzyme classes provides a tremendous goldmine for discovering improved versions of enzymes with known functions as well as for finding completely novel enzymes. With the growing collection of biocatalytic reactions the retrosynthetic thinking from chemical synthesis can be applied to biocatalysis as well.

Once the feasibility of a biocatalytic reaction has been proven, up- and downscaling experiments have been useful for engineering the most adequate process design. In the case of the first large-scale biocatalytic Baeyer-Villiger oxidation, the debottlenecking of the substrate feed and product recovery, final purification and overcoming thermodynamic limitations have been essential in establishing bioprocesses with high yields of enantiopure products [1,2]. These downscaling experiments in conjunction with new analytical techniques have proven useful also in the case of asymmetric synthesis of natural compounds. Spatial and temporal organisation of biocatalysts, reactants or products is another interesting engineering option for biocatalytic process design.

The interdisciplinary character of the dead ends and locks between chemistry, biology and engineering requires investigations of the interfaces. Communication across scientific and technological disciplines including the value creation perspective is important for the development of a better synthesis of the final product-in-the-bottle. Whether the successful problem solution will come from the engineering of substrates, reaction media, process conditions or from the search for better and new enzymes, progress in the understanding of the molecular mechanisms of enzyme action will be key for the further development of the science of synthesis with its challenges towards the more difficult and more complex target molecules [3].

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MICRO AND NANO SYSTEMS (MINAS) RESEARCH AT LAAS-CNRS

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(<http://www2.laas.fr/laas/2-5252-MINAS-Area.php>)

The MINAS research is devoted to micro and nano systems design, fabrication and characterization This research is distributed into 7 research groups, including 78 researchers and 117 PhD students :

- Integration of energy management systems
- Micro and nano system for wireless communication
- Microwave integrated devices and systems for telecommunication
- Photonics
- Nano-bio-systems
- Microdevices and microsystems for detection
- Nano engineering and system integration

This research is focused on the study and development of multidisciplinary and multifunctional micro and nano systems :

- Micro and nano technologies integrating new functional organic and inorganic materials, heterogeneous integration technologies
- Multi-physical and multi-scale modeling for micro and nano systems, bio-nano-technologies and ultimate electronics
- Complex microsystems design and virtual prototyping
- Microsystems reliability
- Micro and nano systems for detection and actuation
- Micro-nano-fluidics and nano-bio-systems
- Optical sources and functions for photonic integration, nano-photonics, MOEMS and micro-optics
- Power-electronics components and electrical energy management integration systems
- RF MEMS and integrated microwaves circuits

The application fields are very large including :

- Telecommunication
- Pharmacological research and bio-medical diagnosis
- Aeronautics and space
- Domotics
- Adaptative and ophthalmic optics
- Metrology

Technological development and manufacturing are operated in a 1500m² clean room (28 engineers and technicians) (<http://www2.laas.fr/laas/2-6846-Basic-Technological-Research.php>) Characterization of micro and nano-systems are performed in a 800m² instrumental platform (20 engineers and technicians) where electronic, radio frequency, optical and bio-chemical characterizations can be addressed.

PROCESSING AND PROPERTIES OF POLYMER NANOCOMPOSITES WITH CARBON NANOTUBES AND OTHER NANOOBJECTS

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Carbon nanotubes (CNTs), carbon nanofibres (CNF) and grafenes are carbon structures with extraordinary mechanical, chemical and electrical properties. These unique properties make these carbon nanoobjects (CNOs) extremely valuable in a wide range of end-use applications. In particular, the use of CNOs as nanofillers of thermoplastic and thermosetting polymer matrices allows the production of innovative materials with breakthrough structural and functional properties. However, the achievement of these properties requires a careful definition of processing routes and conditions able to produce nanocomposites with designed and controlled nanofiller dispersion, orientation and alignment. It is the aim of this research work to consider the approaches to controlled processing and chemical functionalization of CNOs and to account for the advances that have been produced so far in the processing of these innovative materials.

More specifically, due to their exceptional mechanical, thermal and electrical properties, carbon nanotubes (CNTs) have been used in the last decade for the development of high performance nanostructured materials. Since their discovery in 1993 the research in this exciting field has been in continuous evolution, being most of the research focused on the assessment of the CNT properties and the development of advanced structural composites based on CNTs. Single-walled carbon nanotubes (SWNTs) are considered as the simplest member of the family of CNTs, consisting of one graphitic sheet, which has been rolled up into a cylindrical shape. Depending on the arrangement of the hexagon rings along the tubular surface, CNT can be metallic or semiconducting. However, the incorporation of nanotubes is not a trivial task mainly if a good dispersion for a chemical grafting to the polymer matrix are mandatory to maximize the advantage of nanotube reinforcement. In fact, the affinity to adhere to each other, renders as-grown SWNTs intractable and indispersable in common solvents.

On the other hand, it has been demonstrated that CNT can be made soluble when they interact with different classes of compounds. The key challenges that are in the way of realizing composites made out of carbon nanotubes are securing a reliable control over their surface chemistry through either covalent or non-covalent modification and achieving dispersion.

Here we report some examples of nanocomposites with CNTs highlighting a meshwork of interactions between the mechanical, electrical and optical properties of CNTs and the interface with the polymer matrix with the aim to offer an overview on the approaches of chemical functionalization of CNTs and to account for the advances that have been produced so far. The use of electrical and magnetic fields as processing aids for the production of aligned nanocomposites is also reported.

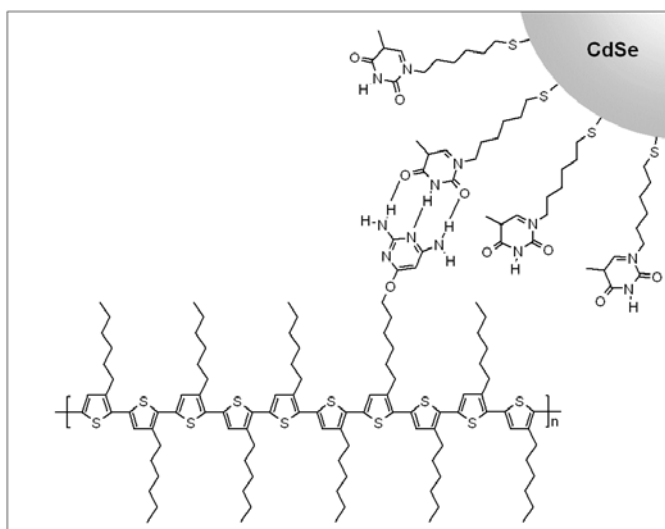
NANOCOMPOSITES OF SEMICONDUCTOR NANOCRYSTALS AND ELECTROACTIVE POLYMERS VIA BIO-INSPIRED MOLECULAR RECOGNITION

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Nanocomposites of semiconductor nanocrystals and electroactive polymers are new materials whose spectroscopic, electronic, redox and electrochemical properties can be precisely tuned to meet specific requirements for their application in a given electronic or electrochemical device. From this point of view the control of their supramolecular organization is of crucial importance. The most important methods of the preparation and processing of supramolecularly ordered nanocomposites will be reviewed. This will involve physical methods like epitaxial directional crystallization of the polymeric component [1] and chemical ones such as nanocrystals' initial ligands exchange for the polymeric ones [2], grafting of electroactive polymers to nanocrystals' surface through a linker ligand [3] *etc.* Special attention will be paid to the preparation of molecular hybrids of semiconductor nanocrystals and electroactive polymers which self-assemble *via* molecular recognition (a representative example is shown in *Scheme 1*) [4]. An interesting feature of the described system is the possibility of its processing using the layer by layer (LbL) technique [5].



Scheme 1: Molecular recognition between 1-(6-mercaptohexyl)thymine capped CdSe nanocrystals (Thy-CdSe) and diaminopyrimidine (functionalized poly(3-hexylthiophene) (DAP-P3HT))

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SYSTEMS BIOTECHNOLOGY AS A CHANCE FOR INTEGRATION OF BIOLOGY AND ENGINEERING

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Differences in education backgrounds of engineers and biologists have been presented with the emphasis of advantages and disadvantages of both professionals approach to solving of contemporary problems in biotechnology.

Before the systems biology was defined the roles and challenges of bioprocess and biochemical engineering, metabolic engineering and bio-informatics were demonstrated. Some examples of holistic approach to description of the complex system such living cell presents were given. Pictorial description of e-cell and erythrocyte was shown.

The newest achievements of systems biology with particular attention focused on engineering approach to biological system were presented. The evolution of the system biology to synthetic biology or biological engineering, as well as the perspectives of this fast developing discipline was also depicted.

The important conclusion of this presentation is that systems biotechnology is the real chance for integration of life sciences and engineering.

**METABOLIC MODELLING OF A TWO-SPECIES CULTURE
COMPRISING A 1,3-PROPANEDIOL PRODUCER *CLOSTRIDIUM
BUTYRICUM* AND A METHANOGENIC ARCHEON
METHANOSARCINA MAZEI.**

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Clostridium butyricum is an anaerobic bacterium capable of fermenting glycerol into 1,3-propanediol, which is an attractive monomer for the manufacturing of new polymers. As typically in many other fermentation processes, this bioprocess is accompanied by the excretion of inhibitive by-products: acetate, formate and butyrate. In order to relieve by-product inhibition and at the same time to make use of them for energy production a novel mixed culture system comprising *Methanosarcina mazei* and *C. butyricum* has been proposed. In order to know whether such a syntrophic-like growth of these two organisms allows an efficient utilisation of the inhibitive by-products and to find the optimum conditions for this, a conceptual study of this two-species culture has been performed in this work with the use of metabolic modelling [1].

The metabolic networks for these two microorganisms were reconstructed on the basis of genomic information and physiological data [2-4]. The individual networks were first tested separately for their conformity with experimental data available in literature [5,6]. Then several scenarios were computed with the use of optimisation procedures to determine *M. mazei* preferences in scavenging acetate and formate under various substrate availability, including situation when methanol, which is an impurity in the raw glycerol from biodiesel plants, is present in the system. The calculations revealed that if methanol was present, methane production from methanogen could be increased by about 130%. Furthermore, it was found that *M. mazei* was capable of utilising *C. butyricum* by-products with good efficiency. On average, over 70% of acetate was scavenged by *M. mazei*. The simulations also revealed that switching of *M. mazei* metabolism towards methanogenesis and avoiding extensive biomass growth of *M. mazei*, especially in the presence of hydrogen, assure efficient operation of this two species system. Furthermore, if *C. butyricum* produced no hydrogen, acetate utilisation would be preferred.

Acknowledgements

I wish to thank to Prof. An-Ping Zeng and his co-workers from Technische Universität Hamburg-Harburg (TUHH) for invitation to Department of Bioprocess and Biosystems Engineering of TUHH and fruitful discussions concerning the subject of this presentation

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SMALL RNA MOLECULES AS UNIVERSAL AND USEFUL REGULATORS OF GENE EXPRESSION

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Gene silencing directed by small RNA molecules is a powerful, evolutionary conserved mechanism. Intensive investigations in this field have taken place since the discovery of RNAi phenomenon (RNA interference) about a decade ago [1]. Short RNA duplexes (siRNA, short interfering RNA) play a central role in this mechanism by guiding a multiprotein complex with endonuclease activity to the target mRNA. Shortly after initial studies, the effect was induced in human cells and first therapeutic trials have been conducted in 2004. Furthermore, the possibility to enhance pharmacokinetic properties of siRNAs by chemical modifications makes them quite universal gene silencing tools [2].

Vigorous attention driven to small noncoding RNA (sRNA, ncRNA) involved in the gene expression regulation have revived the research in these field in prokaryotic organisms as well. There are several RNA regulators in bacteria cells, known since 1970's, but an overflow of new discoveries of ncRNAs arose lately. At present over 70 of such molecules have been found in *Escherichia coli* genome [3].

Bacterial regulatory RNA act in two basic ways: via interaction with proteins functioning as gene expression regulators or by binding with mRNA (in RBS, UTR or promoter regions). There are growing evidences of crucial role of ncRNAs in known regulatory pathways such as two component systems (TCS). An interesting example of such pathway is so called quorum sensing (QS), responsible for "social behaviour" (e.g biofilm formation) of microbes. In *Vibrio cholerae* and *Salmonella typhimurium* regulatory influence of CsrA/CsrBCD system (regulatory protein/RNA partners) on QS-dependent biofilm formation was shown [4]. An introduction of vectors coding RNA regulators into bacterial hosts gives possibility to influence complex regulatory pathways in a simple way. Proper expression of RNA molecules is much less complex than proteins, and is more rapid as well.

Our research is focused on *Gluconacetobacter xylinus* productive strain, used in IBT for cellulose biosynthesis. Recent evidence of QS system functioning in *G. intermedius* [5] have driven our interests towards identification of crucial genes involved in QS as well as genes of conserved proteins, interacting with regulatory RNAs in *G. xylinus*. Preliminary results will be discussed.

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SYNTHESIS AND CHARACTERISTICS OF BIOMATERIALS FOR SPECIFIC MEDICAL APPLICATIONS

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Over 95% of the current drugs are characterized by poor pharmacokinetic and biopharmaceutic parameters. Considering this, an urgent need arises to develop more efficient carrier systems for the targeted drugs, acting exclusively on the diseased organ/tissue and not affecting healthy cells. The development of such system would increase the drug potency and at the same time minimize its side effects. The project focuses on two areas of bionanotechnology – the targeted drug delivery and imaging.

Nanoparticles functional in imaging and the delivery of active compounds to the pathologically-altered tissue fragments will be constructed based on superparamagnetic metal oxides coated with gold. The particles will carry proteins recognizing tumor cells (via interaction with cancer-specific markers), as well as cytotoxic agents. In addition, organic linkers will be developed, allowing for the specific display, delivery, release and activation of therapeutic compounds in pathologically-modified sites.

To achieve this objective, an extensive repertoire of methods will be used from the areas of material chemistry, physical biochemistry, molecular biology (including phage display), cell biology and molecular modeling.

APPLICATION OF BIOCATALYSIS TO THE SYNTHESIS OF PHARMACEUTICALS

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Biocatalysis is a methodology of growing importance for the synthesis of pharmaceuticals, resulting in the establishment of many successful synthetic protocols [1]. Main reason for this is the enormous selectivity of biocatalysts. For most applications native and immobilized enzymes are used. The importance of enzyme used as a biocatalysts for the synthesis of key intermediates in drug synthesis will be presented on selected examples. Special attention will be paid to enzyme role and importance of immobilization procedures for biocatalyst activity and selectivity [2,3,4]

This work was financially supported by Polish State Committee for Scientific Research, Grant N405 007 31/0544.

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BIOINFORMATICS IN PROTEIN ENGINEERING: ALTERATION OF RESTRICTION ENZYME SPECIFICITY GUIDED BY BIOINFORMATICS

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Type II restriction endonucleases (REases) comprise one of the largest group of experimentally characterized enzymes. They recognize and cleave DNA sequences with very high specificity and *in vivo* are accompanied by DNA modification methyltransferases with similar specificities that protect the host DNA from cleavage. Among more than 3700 known REases, so far only 270 distinct sequence specificities have been characterized. On the other hand, there are 4096 different combinations of a 6-base pair recognition sequence alone. For many applications of REases in molecular medicine and biotechnology such a limitation of the recognition sequence set is detrimental. One proposed approach to overcome it, is to create enzymes with new specificities by means of protein engineering (e.g. by mutagenesis). Protein engineering of REases is however challenging due to limited coverage of known enzymes by structural data, high diversity of sequences, structures, and catalytic mechanisms, as well as the presence of elaborate networks of interactions that couple substrate recognition with cleavage activity in individual enzymes.

We present preliminary results of two case studies: engineering of REases guided by bioinformatics. We have focused on enzymes containing unspecified nucleotides in their recognition sequences: Bsp6I (GCNGC) and NlaIV (GGNNCC). Selecting enzymes with such sequence specificities allowed us to avoid two potential problems: i) none of the existing protein-DNA contacts have to be eliminated or changed (only new contacts should be introduced) and ii) the bacterial host with the wild-type DNA methyltransferase will be protected from the activity of variants of the enzyme with a novel, more stringent specificity. We have used bioinformatic tools to build structural models of the target enzymes, and supported the validity of these models by experimental analyses. The structural models were used to identify for mutagenesis such regions of the enzymes, which could potentially develop new contacts with central nucleotides (unrecognized by the wild type enzymes).

Bsp6I is a dimer that recognizes a non-palindromic DNA sequence. We have engineered a system, which allows independent manipulation of each subunit, either through tandem purification of differently tagged two coexpressed recombinant proteins or in a single-chain variant of the REase. We have obtained variants with a preference towards GGWCC (W=A or T) sequence, which can either introduce double stranded cuts (as the wild type enzyme) or act as sequence and strand specific nickase.

In case of NlaIV, several mutant libraries were made by orthogonal saturation mutagenesis of selected regions, with mutagenic oligonucleotides synthesized via the split-and-mix strategy. These libraries were expressed in a compartmentalized *in vitro* transcription-translation system and screened for GGWWCC cleavage preference in a novel *in vitro* selection system. Our system allows for iteration of the selection process entirely *in vitro*, without cloning or *in vivo* plasmid propagation. We have obtained several variants with altered sequence preference.

Our preliminary data indicate that integration of bioinformatics analyses (in particular protein structure prediction) with techniques of protein engineering is a promising strategy in this important and challenging field of biotechnology.

BREAST TISSUE DIAGNOSIS BY RAMAN SPECTROSCOPY

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We would like to present our recent results on normal, malignant, and benign breast tissue by Raman spectroscopy for 100 patients and compare them with the results of histopathological analysis to estimate the sensitivity and specificity of the method. The data are statistically analyzed with PCA methods. We demonstrate that lipid and carotenoid molecules play a key role in activity of human membranes and decide about the health-disease balance in living creatures. Our recent papers [1-3] on cancer diagnostics by Raman spectroscopy demonstrates its power as diagnostic tool for breast cancer diagnosis. The results demonstrate the ability of Raman spectroscopy to accurately characterize breast cancer tissue and provide evidence that carotenoids and lipids of the tissue play an essential role as a Raman biomarkers that are able to distinguish between normal, malignant and benign types. We discuss molecular mechanisms of energy dissipation in normal and malignant tissue and the role played by carotenoids including ability to act as lipid-phase anti-oxidants, and the light harvesting antenna that can protect system from oxidative damage, as well as to act as upregulator of junctional communication in connexins. To answer the questions about the photostability we have to understand mechanisms of energy dissipation upon an optical excitation [4].

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ULTRAFAST ENERGY FLOW AT THE PHOSPHOLIPID-WATER INTERFACE

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We report on energy dynamics at the water/lipid interface. Femtosecond infrared one- and two-color pump-probe experiments were used to investigate vibrational relaxation dynamics of C-H stretch modes in the lipid alkyl chains of Dipalmitoyl phosphatidylcholine (DPPC) and O-H stretch modes of water at the water/lipid interface for a controlled humidity of the sample.

The detailed vibrational dynamics of alkyl chain modes of lipid, interfacial water and mutual interactions has been elucidated. The results reveal that coherent energy transfer occurs from the excited state of the O-H stretch mode of water to the CH₂ groups and the terminal CH₃ groups in the lipid alkyl chains. Vibrational relaxation of water is significantly slower than that in bulk water. The vibrational lifetimes of C-H stretch modes in the lipid alkyl chains of DPPC both in the CH₂ groups and the terminal CH₃ groups decrease when the water content of the sample is lowered.

OPTICAL AND ELECTRICAL PROPERTIES OF SEMICONDUCTING POLYMERS LOADED WITH GOLD AND SILVER NANOPARTICLES

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Noble metal nanoparticles (NP) were proposed to improve performance of many optoelectronic devices due to the resonance interaction of surface plasmons with incident light or with excited states of attached functional molecules. In organic photovoltaic devices they can (i) modify the photoinduced charge transfer from donor to acceptor, (ii) modify the deactivation processes of excited molecules and (iii) locally increase optical absorption due to surface plasmon extinction and/or increased electric field in the vicinity of nanoparticles. The properties of π -conjugated polymer nanocomposites, based on MEH-PPV or soluble polythiophenes and containing Ag and Au NPs prepared by various procedures will be shown. The derivatization of the polymers by imidazolium, pyridinium or carboxylic groups led to a better adsorption abilities of the polymer on the NP surface. Laser ablation was tested as an efficient method of the preparation of NPs with clean surface capable of better interaction with the adsorbate. The presence of fractal aggregates were detected in the nanocomposites in which very strong enhancement of local optical fields appears. In the photovoltaic devices the controlled space distribution of NPs has to be optimized to balance the plasmonic effect, possible shunt resistance and the absorption losses resulting in inefficient energy dumping.

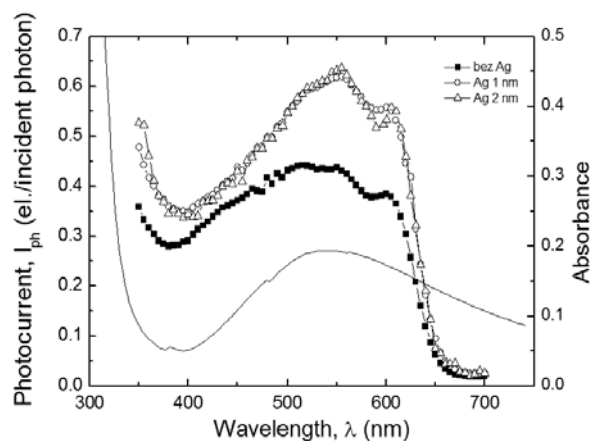


Fig. 1: Spectral dependence of the short-circuit photocurrent of P3HT/PCBM bulk heterojunction with an interfacial layer of nanoparticles obtained from vacuum deposited Ag layer of thickness 1 nm (\circ), 2 nm (Δ), and without Ag nanoparticles (\blacksquare). Full line – surface plasmon optical extinction of Ag nanoparticles deposited on ITO electrode.

An interesting improvement of the photovoltaic effect detected on bulk heterostructures based on poly(3-hexylthiophene) and soluble derivatives of C_{60} , with a single interfacial layer of Ag nanoparticles, prepared by spontaneous aggregation from thin vacuum deposited layer of silver of typical thickness 1 -2 nm, is shown in Figure 1. From the optical spectra of a reference Ag nanoparticle layer deposited on ITO glass substrate the presence of surface plasmons is clearly evidenced, as well as the enhancement of the short-circuit photocurrent in the same spectral region.

Acknowledgement:

Financial support No. KAN100500652 of the Grant Agency of the Academy of Sciences of the Czech Republic, Program Nanotechnology for Society, is greatly acknowledged.

SOLUTION ZONE CASTING; A METHOD FOR FABRICATION OF ORIENTED ORGANIC LAYERS AND MICROPATTERNS FOR OPTOELECTRONICS.

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Achievement of macroscopic scale long-range order (and thus orientation) in organic conductors and semiconductors is of a great importance in their applications in electronics and optoelectronics. The presentation will describe *zone casting* - a universal method for the solution casting based fabrication of oriented anisotropic layers of molecular materials which does not require patterned substrates[1-6]. In this method, solution is continuously supplied onto the substrate withdrawn at a controlled rate and the solvent evaporates from the surface of meniscus formed between a flat nozzle and the substrate. Due to the presence of the gradient of the solute concentration, its solidification proceeds within the narrow zone localized in the meniscus. In this way solute molecules can be self-assembled at surfaces into different anisotropic nanostructures (columns, rods, lamellae or crystals) uniaxially aligned parallel to the substrate. Under some conditions various phenomena like e.g. dewetting, fingering instability, stick-slip motion etc. come into play leading to various periodic interruptions in the film deposition[7]. Examples of continuous and micropatterned layers of different materials such as low molecular weight (semi)conductors, chromophores, discotic molecules and block copolymers, which can successfully be processed using this technique, are shown. Some of the obtained layers were already shown to have good properties as active layers in field effect transistors [8-11].

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ORGANIC AND HYBRID MATERIALS FOR PHOTOVOLTAIC APPLICATION

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The most of the present world production of photovoltaic (PV) cells is based on crystalline silicon. However, the high-temperature fabrication routes to single-crystal and polycrystalline silicon are energy intensive and expensive. The search for alternative solar cells is therefore focused on thin films of organic (based on π -conjugated polymers) and hybrid (organic-inorganic) nanocomposites, that can be prepared by cheaper, e.g. solution based methods. The examples of such structures are represented by interpenetrating networks of n -type and p -type organic semiconductors that form so called bulk heterojunctions, as well as by dye-sensitized nanocrystalline inorganic semiconductor layers [1].

Nanocomposites with enhanced surface of p - n junction were prepared with use of so called "reticulate doping" method. The idea behind the term "reticulate doping" is that the low molecular weight "dopant" (n -type) forms a separate crystalline phase, which penetrates a polymer (p -type) matrix or at least its surface layer. We have found, by means of surface potential decay measurements, that high degree of crystallinity of the n -type component improves its transport properties and brings an increase in photogeneration efficiency at the p - n junction.

Hybrid organic-inorganic structures, applied in dye sensitized solar cells (DSSCs), combine the best properties of organic (e.g. processability) and inorganic materials (e.g. good charge transport) properties. A typical DSSC consists of nanocrystalline TiO_2 electrode covered with a mono-layer of sensitizing dye, a redox electrolyte (e.g. I^-/I_3^-) and a counter electrode such as platinized conductive glass. Platinum is known to possess high catalytic activity for reduction of I_3^- to I^- in the redox electrolyte, which is necessary, for proper cell performance. On the other hand, Pt is one of the most expensive components in DSSC. Therefore, the use of non-insulating plastic materials, which belongs to the class of so-called conjugated polymers, instead of Pt is expected to reduce production costs, particularly in case of large-scale manufacturing. In our work, we applied completely plastic counter electrode as PEDOT:PSS on polyester substrate instead of platinized conducting glass. Our main attention was focused on studies of behaviour of such plastic counter electrode in the presence of I^-/I_3^- redox couple. In order to probe chemical and electronic properties of PEDOT:PSS foil, X-ray photoelectron spectroscopy was used as a powerful tool to study the atomic composition of the surface.

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ALL-ORGANIC, FLEXIBLE FIELD-EFFECT-TRANSISTORS: TOWARDS 'PLASTIC ELECTRONICS'

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Large area organic electronics requires technologies with only few production steps, yielding in a reproducible way materials with well defined morphology and properties. In general, control of organisation of molecules in layers made of organic semiconductors is crucial for fabrication of organic opto-electronic devices, e.g. photovoltaic diodes or field effect transistors [1]. It has been proven that strong π - π stacking is an effective approach to one-dimensional nanostructures for aromatic organic compounds to enhance the charge carrier mobility along the stacking direction.

Among methods allowing to prepare ordered structures, these based on self-assembly phenomenon are highly valued because of their simplicity and low cost. The solution based methods, the so-called zone-casting and two-step reticulate doping[1-3], allow to produce highly oriented layers of organic semiconductors, as illustrated by two examples in this presentation. Flexible organic field effect transistors were fabricated using an insulating polymer, Parylene C, simultaneously as the dielectric layer and as the substrate. Thin films of Parylene C were obtained by chemical vapour deposition, whereas ordered layers of organic semiconductors, tetrakis-(docosylthio)-tetrathiafulvalene, were prepared by the zone-casting technique. The zone-cast layers of organic semiconductors exhibit unidirectional orientation on large area, *ca.* 20 cm², as shown by XRD, AFM polarized Raman Microscopy and FET characteristics. The second approach consists in the *in situ* crystallization of organic semiconductor on surface of the polymer film. The bi-layer composites with crystalline layers of low molecular weight semiconductor (perylene derivative) grown on polymer matrix (poly(3-hexylthiophene) were produce according to the two-step reticulate doping procedure. The crystallization of the dopant occurs in the surface layer of the polymer film, yielding uniaxially arranged crystalline domains with anisotropic optical and electrical properties.

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INTELLIGENT MICROSYSTEMS (IMEMS) – COMPUTER MODELS

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Micro-Electromechanical-Systems (MEMS) technology has generated a significant interest of academic, research and business sectors. MEMS are a combination of mechanical and electrical features on a very small scale. The design, analysis, and control of micro-electromechanical systems are inherently geometric in nature. Accelerometers are important devices in the range of variety applications such as air bag actuation (by Analog and Berkeley Sensor and Actuator Centre), micro robots, etc. Silicon inertial sensors were initially used in military applications before finding a major new market at the end of the 1980s as airbag sensors in cars. Micromachined sensing elements for accelerometers can be fabricated either by bulk micromachining, surface micromachining or the LIGA (German abbreviation for Lithografie, Galvanoformung, Abformung) process. The two most commonly used methods for detecting the position of the seismic mass are piezoresistive or capacitive signal pick-off. Analytical models are exploited to define coupling between different directions of motion, derived by means of virtual principle work. Finite element analyses are done for a range of suspending spring, for different spring structures, in order to verify the models and determine the validity range as well.

A good strategy in design of MEMS should capture the essential static and dynamic behaviour of the device using a minimal set of equations, which are in terms of the physical design parameters and material properties. Analytical models are useful to describe coupling between different directions of motion, and are derived by use of the energy methods. The effect of spring mass on resonant frequency of different modes is taken into account by an “effective mass model”.

In the design of microsystems, sophisticated CAD systems, based on Finite Element Method (FEM), like OPERA from Vector Fields, COSMOS and ANSYS, are exploited for modelling and simulation the behaviour of the system components with high accuracy. Finite element analyses is the most commonly used methods for numerical mechanical and electrostatic simulations. Unfortunately, FEM simulations are time consuming. In the conceptual design stage modelling, simulation and analysis tools should consider the functional interaction between domain specific subsystems.

In author opinion, a modelling and simulation tool for complex MEMS systems should be able to handle Object-Oriented Models in multiple physical domains, since the model of a mechatronic system consists of the integration of submodels in multiple physical domains and the information domain. Both, mechanical and electric models give the input data for defining the Object-Oriented Model (OOM), based on Matlab-Simulink platform, fulfilling the general demand of dynamic behaviour simulation of comb drive structure. A Simulink library of accelerometer elements (springs and comb-drives and additional components) has been created to model the accelerometer subsystems and to simulate complete system behaviour.

A novel complex strategy in computer modelling of accelerometer, based on solid modelling, is proposed by authors in this paper. This methodology consists of the following general steps:

- Creation mathematical model of 3D structure,
- Parameterized model to speed up introducing accelerometer geometry,
- Creation the complex electromechanical models of accelerometer dynamic behaviour (system of electric and mechanical partial differential equations – based on model lumped parameters).
- Creation Library of Object-Oriented accelerometer components.

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TECHNOLOGY OF SILICON CARBIDE – POLISH GOVERNMENT PROJECT

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Recently, the investigations dealing with the silicon carbide are more and more intensive. It is caused by its extremely attractive parameters in comparison to silicon ones. It is characterized by the larger band gap, the better heat conductivity, the larger electron saturation velocity and the larger critical electric field strength. These parameters, potentially, allow manufacturing devices characterized by ratings unattainable for the devices manufactured from silicon or other semiconductors. The large critical electric field strength allows getting p-n junctions with the breakdown voltage larger than 10 kV. The large band gap makes possible manufacturing low noise devices or devices working at high temperatures exceeding even 700°C whereas the large saturation electron velocity makes SiC an excellent candidate for high frequency devices with the possible maximal frequency reaching THz.

The basic obstacle in practical use of silicon carbide consists in different, very often extreme, demands concerning the technology processes. It causes that the technologies well known in the silicon technology occur often to be inappropriate in the case of silicon carbide. The Polish National Silicon Carbide Program is aimed at solving some of these problems. It consists of three thematic tasks aimed at SiC in bulk and substrate form, SiC device manufacturing and SiC devices application, respectively.

The first task is dominating in the program. Its main project is devoted to work out the technology of 6H:SiC and 4H:SiC monocrystal bulks produced from silicon carbide powder using the methods basing on Lelley approach. Other projects of this task concern next steps necessary to obtain 6H:SiC and 4H:SiC polished substrates with and without an epilayer, characterized by the quality satisfying device producers.

The second one covers projects dealing with device manufacturing. Since the well-characterized substrate is a base for any research activity, a few projects is concentrated on the SiC structures characterization methods. Others deal with the technology problems like the technology of selective ion implantation, which is the key process for MISFET technology as well as the termination in high voltage devices, the technologies of electrical contacts and packaging technology taking also into account the problems resulting from SiC application in high temperature electronics. In this task, the separate group is formed by the projects aimed at the technology of particular devices with the final goal to deliver the demonstrators of these devices. They deal with Schottky diodes, PiN diodes, MISFET and JFET transistors manufactured on SiC substrates as well as with high-frequency HFET transistors and Schottky diodes manufactured as AlN/SiC heterostructures.

The third task covers two projects concentrated on the investigations of advantages and disadvantages resulting from the application of SiC devices in power electronics circuits. Basing on the commercial available elements like Schottky diodes and MESFET transistors mainly, they cover the investigations of device features from the point of view of their influence on design process and work conditions in the real power electronics equipment.

SCANNING TUNNELING SPECTROSCOPY AND RAMAN SPECTROSCOPY OF MONO-, BI- AND TRI- GRAPHENE LAYERS DEPOSITED ON CONDUCTIVE AU/CR/SIO₂/SI SUBSTRATE

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In the first part of our talk short introduction to physics of graphene will be given including quantum electrodynamical (QED) consequences of linear dependence of energy of electrons as a function of wave vector. The basic applications of graphene in electronics will be briefly outlined.

The second part of our talk deals with graphene devices. Graphene devices require electric contacts with metals, particularly with gold. Scanning tunneling spectroscopy studies of electron local density of states performed on mono-, bi- and tri- graphene layer deposited on metallic conductive Au/Cr/SiO₂/Si substrate shows that gold substrate causes the Fermi level shift downwards which means that holes are donated by metal substrate to graphene which becomes p-type doped [1,2]. These experimental results are in good accordance with recently published density function theory calculations [3]. The estimated positions of the Dirac point show that the higher number of graphene layers the lower Fermi level shift is observed.

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FROM MICROSYSTEMS TO NANOTECHNOLOGY – TUL DMCS PROJECTS

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The silicon micro- and nanosystems are nowadays one of the most rapidly developing branch of electronics. Particularly it refers to this sort of entities in which the incoming signal sensors are integrated with circuits responsible for data processing, analogue to digital converters, buffers, memories etc. The origin of sensed signals can be of various kinds. There are sensors of heat, concentration of ions in certain solution (ISFET sensors), acceleration, infrared radiation etc. This is connected with very fast development of micro- and nanoelectronic technologies, which are supported with design kits.

Modern electronic micro- and nanosystems often comprise various sensors whose operation principle is based on different physical phenomena not necessarily purely electrical ones. Specialised networks dedicated for continuous monitoring of air, water and soil pollution, which are currently under development in many industrialised countries, might serve as good examples of such systems [1,2]. For proper Computer Aided Design (CAD) of these complex systems, engineers need adequate device models and simulation tools rendering possible multidomain simulation [2].

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METHODS OF COMPUTER PHYSICS USED TO SIMULATE AN OPERATION OF DIODE LASERS

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During the presentation, methods of computer physics will be presented and their application to model an operation of modern vertical-cavity surface-emitting diode lasers will be explained. Computer physics methods used to simulate some physical phenomena or to carry out so called physical experiments are the methods, in which a computer plays an essential role. Computer experiments are used to simulate physical phenomena when their pace is too rapid, when sizes of a device under consideration are too small or when normal physical experiments are too expensive or too dangerous for people or an equipment. In the case of diode lasers, they sizes are definitely too small and preparing one device for measurement purposes is too expensive, therefore computer experiments instead of normal ones are justified.

POLYCRYSTALLINE SOLAR CELLS FOR BIPV APPLICATIONS

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Big potential of cadmium telluride in photovoltaic applications was proved by many researchers among last decade [1,2]. These cells, in their typical construction, based on CdS/CdTe semiconductor heterojunction, are expected to be the future generation devices owing to their good mechanical and optical parameters, and relatively low production cost. However the monolithic CdS/CdTe cells are now entering the early production phase, there are still the possibilities of expanding of their capabilities by exploring of the new application fields. Basing on this idea authors proposed the implementation of modified CdS/CdTe cell structure in universal, attractive application called BIPV (Building Integrated Photovoltaics) [3, 4]. The CdTe cell construction gives the opportunity of achieving the goal, under the conditions [5] of the proper technology modifications, as well as proper substrate implementation, based on the material studies, which is the main goal of the paper. Additionally, unique properties of CdS/CdTe cell make possible the closest integration with the architectonic element, delivering the PV product of a new quality standard. Thus the idea of the fully integration of PV elements with the surrounding environment [6] may be practically realized. Realization of this concept is also in the scope of presented research.

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**STUDIES ON BIOMATERIALS
AND NANOSTRUCTURED POLYMERS
IN THE CENTRE OF MOLECULAR AND MACROMOLECULAR
STUDIES OF THE POLISH ACADEMY OF SCIENCES**

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Comprehensive survey of studies on biomaterials and nanostructured polymers that are carried on in the Centre of Molecular and Macromolecular Studies PAS (CMMS PAS) will be presented during the lecture. There are several research groups in Departments of Polymer Chemistry, Polymer Physics and Engineering of Polymer Materials concentrated on studies related to the title area. Below there are listed major subjects of these studies:

1. Controlled synthesis and detailed characterization of star-shaped biodegradable macromolecules
2. Synthesis of inorganic-polymer nanohybrids with controlled morphology and their application as building blocks of polymer scaffolds
3. Synthesis of hydrophilic-hydrophobic block copolymers and their self-assembly into nanoparticles.
4. Direct synthesis and physicochemical methods of fabrication of biodegradable nano- and microparticles and their application for drug delivery.
5. Colloidal particles for diagnostic applications
6. Fabrication of one-macromolecule thick interfacial monolayers with properties adaptable to environment.
7. Macromolecules on silica wafers – materials for biosensors
8. Nanolayers on various substrates by zone-casting and by chemical vapour deposition (CVD) methods
9. Polymers with antimicrobial interfacial properties
10. Formation and properties of nanostructured polymers by dedicated processing methods
11. Polymer based nanocomposites

Presentation will be arranged in a way allowing identification of research topics that would benefit from close and intensive collaboration with other groups representatives of which will participate in the workshop. In particular we expect that other teams with complementary expertise would use our presentation as the basis for development of long-lasting common studies arranged into joint projects.

SHEAR-INDUCED CRYSTALLIZATION OF ISOTACTIC POLYPROPYLENE BASED NANOCOMPOSITES WITH MONTMORILLONITE

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Shear-induced isothermal crystallization in iPP based nanocomposites with organo-modified montmorillonite was followed by light depolarization technique. Prior to the crystallization, samples were sheared at 1 or 2 s⁻¹ for 10 s in a plate-plate system at crystallization temperature of 136 °C. After isothermal crystallization structure of the specimens was investigated by light microscopy and electron microscopy, X-ray techniques and IR spectroscopy. Shearing caused enhancement of the nucleation and acceleration of crystallization in the compatibilized nanocomposites with the clay. Clay exfoliation was found to play an important role in acceleration of the shear-induced crystallization. The sheared samples exhibited only weak orientation of a crystals with (040) crystallographic planes parallel to shearing direction that resulted probably from a small population of oriented crystals that formed due to shear-induced orientation of iPP chains and served as nuclei for further nearly isotropic growth. In addition, shear-induced nonisothermal crystallization of the materials was studied. Shearing at 10-40s⁻¹ for 10 or 20s was applied during cooling of molten samples at 160, 150 or 140 °C. It was found that shearing increases nonisothermal crystallization temperature of the nanocomposite.

LOW DENSITY POLYETHYLENE-MONTMORILLONITE NANOCOMPOSITES FOR FILM BLOWING

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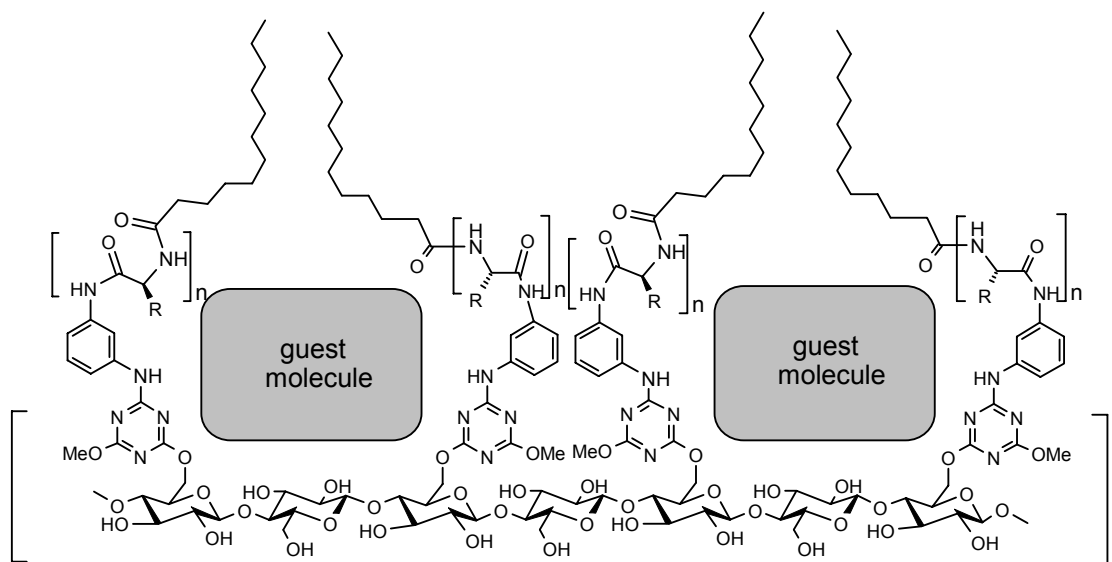
Low density polyethylene nanocomposites were prepared using differently modified montmorillonite (MMT) and different compatibilizers. The best results were obtained for MMT with largest gallery distance. The best system was further optimized by varying the compounding condition. The criteria were mechanical properties nanocomposites, x-ray and TEM proofs of exfoliation. The optimized nanocomposites were used for film blowing. The effect of blow ratio on mechanical properties and oxygen permeation of films was evaluated for two best nanocomposites and two films blown from pristine polyethylene. The texture of crystalline phase of blown films was analyzed by x-ray pole figure technique, SAXS and AFM. The two component texture was detected, the first component related to the molecular orientation of polyethylene by blowing and take-up ratios and the second connected with the formation of free surfaces of the film. The relative stability of crystallinity degree of polyethylene component and stability of long period from SAXS indicated that the compatibilizer was preferentially located around clay platelets and did not enter the amorphous layers of polyethylene. Also the orientation of clay platelets was determined by FTIR using 1080 cm^{-1} band characteristic for Si-O bonds. A clear correlation of oxygen permeativity of blown films with clay platelets orientation and degree of exfoliation was evidenced.

SUPRAMOLECULAR STRUCTURES FORMED BY N-LIPIDATED PEPTIDES IMMOBILIZED ON CELLULOSE. ARTIFICIAL RECEPTORS

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An array of supramolecular structures formed from N-lipidated peptides attached to cellulose via aminophenylamino-1,3,5-triazine was synthesized. The structures thus prepared were prone to self-organization and to formation of monolayer of "holes" and "pockets" in dynamic equilibrium. These structures were found capable of binding small guest molecules very efficiently recognizing the shape, size and polarity of ligands, and thus resembling artificial receptors. Due to the high flexibility of N-lipidated peptides it is expected that the host adjusts its shape to wrap guest molecules most efficiently. The selectivity and rate of binding was studied by using triphenylmethyl dyes. It was found that the selectivity of binding depends on the structure of the peptide and the N-lipidic fragment of the receptor and varies with the structure of the analyte. Even tiny structural changes in guest molecules were detected by monitoring the alteration of the binding pattern [1].



The selectivity of binding was studied by using triphenylmethyl dyes. The interactions of colorless guest with the array were visualized by the subsequent processes of competitive adsorption-desorption of appropriate reporter dye. We found that the selectivity of binding depends on the structure of peptide and lipidic fragment of the receptor and vary with the analyte structure.

The previous studies confirmed that alternation of the binding pattern could detect even tiny structural changes of guest molecules and therefore offer a new tool for SAR studies. An assay of physiological fluids and tissue homogenates has been found useful for diagnosis of thyroid tumors [2].

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ELECTRO-SPUN SMART AND MULTIFUNCTIONAL NON-WOVEN TEXTILES

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Electrospinning is a technique in which polymer solution or melted polymer is pumped through the electrode holes with diameters in the order of 1 mm. After applying the power supply voltage there occurs electrical induction and the solution becomes charged. Consequently, the solution in its entire capacity is given a single fixed potential. Under the influence of the active electrostatic field and the present Coulomb forces, the semispherical drop surface at the nozzle mouth of the capillary is strained into a conical shape (known as Taylor cone), and then it is stretched into a stream and significantly thinned. The polymer is collected on an earthed collecting element. The polymer stream forming mechanism takes approximately 0,0125 ms. The charges that gather on the polymer stream surface, in combination with the stream's surface tension, cause the stream to bend, in effect of which the distance covered by the polymer becomes extended. As a consequence of the active electrostatic field, the fibres so manufactured have the diameters that vary from ten to several hundred nanometres. Electrospinning process needs a polymer in a liquid state, which can be released by melting or by solving. At the Department of Fibre Physics and Textile Metrology the original multi-nozzle stand for electrospinning of polymer solution was build. The effectiveness of 32 nozzles stand is in the range of 5 ml/h-500 ml/h.

In presented work, the electrospinning process was proposed as a method of production of nanofibrous material for sensor and medical application. In a case of material for sensors the unique properties of specially developed conductive polymer composites (CPCs) composed of PEO and carbon nanotubes (CNT) are demonstrated [1,2]. Obtained electrospun non-wovens are characterized by changing the electrical resistance under the influence of selected liquids and vapours.

In a case of medical application as a raw material, the dibutylchitin (DBC) was used. DBC characterises very good biomedical properties, thereof it can be used as a biomaterial [3,4]. It is ease dissolved in common solvents like DMSO or ethyl alcohol. Due to electrospinning of DBC, dependently on the technological parameters of process, different shapes and diameters of fibres were obtained [5,6,7].

Conclusions

The electrospinning is a technique allowing forming the fibrous 3D structures from the whole range of polymers, even from polymers that cannot be processed using classical man- made technologies.

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MOLECULAR AND NANOSTRUCTURAL BIOPHYSICS LABORATORY IN TECHNOPARK LODZ

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Two important facts have to be mentioned as an introduction. The first one, that the TECHNOPARK Lodz has successfully applied for financial support concerning creation of hi-tech laboratories, and the second one, that last December the agreement between the Center for Advanced Technology BioTechMed and the TECHNOPARK Lodz was signed. The agreement concerns creation of the TECNOPARK branch of BioTechMed Laboratories.

This agreement introduces a multistage project open for new ideas and new technologies, and the laboratories are intended to close cooperation with industrial and academic partners. Currently the project is under implementation on two separate levels. The less advanced project has promised financial support from PO-IG structural fund (Operative Project – Innovative Economy) allocated to creation of two laboratories. The first one, being a part of the branch of BioTechMed is the Laboratory of Industrial Biotechnology. The second one is the Laboratory of Hydrogen and Clean Sources of Energy.

The more advanced project, currently in implementation, concerns two laboratories which already have financial support from RPO (Regional Operative Project) structural fund. These are the Laboratory for Testing of Electric Devices and the Laboratory of Molecular and Nanostructural Biophysics. The last one is also a part of the branch of BioTechMed and will be the matter of the presentation.

The main activity of the Laboratory of Molecular and Nanostructural Biophysics will be focused on different aspects of interaction of products of nanotechnology with biological objects. We want to know results of nanostructure contact with molecules, cells and tissues, and we are going to present, to the society and decision makers, well documented effects of nanostructures presence in the environment and biosphere. We want to cooperate with both academia and industry in solving the most hot problems concerning the risk resulting from the presence of nanotechnology products in the surrounding environment. We would like to underline, that we are not against the nanotechnology, we want to support balanced development of nanotechnology and economy but also protect the society from unnecessary health hazard.

The laboratory will consist of several specialist labs:

- cell culture
- cell biology
- biochemistry
- transcriptomics
- proteomics
- biophysics
- personalized medical implants,

all located on a total surface of 650 m² with 15 researchers employed for proper laboratory operation.

The laboratory is interested in a close cooperation with the Centre for Bio- and Nanotechnology of the Technical University of Lodz, and with other research institutions.

SYNTHESIS OF NANOGELS BY RADIATION-INDUCED INTRAMOLECULAR CROSS-LINKING OF SINGLE POLYMER CHAINS

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Polymeric nanogels can be defined either as tiny fragments of water-swallowable polymeric networks or as single macromolecules of particular topology – internally cross-linked polymer coils. They differ from linear polymer chains in many aspects, for instance they are characterized by higher stability of shape and dimensions in solutions and possess the ability to trap smaller molecules within their structure. Nanogels have been intensely studied in the last decade. Their applications will probably mainly focus on nanomedicine (for example as drug delivery systems and vectors for gene therapy).

Most methods utilized so far for synthesizing nanogels require the presence of auxiliary chemicals, such as initiators, cross-linking agents and emulsion stabilizers. A method being developed at our lab utilizes polymer chains and water as the only substrates, with no additives required. Short pulses of fast electrons are applied to dilute aqueous polymer solution and generate instantaneously a number of radicals on each linear polymer chain. Subsequent predominantly intramolecular recombination of these radicals leads to the formation of covalent bonds between chain segments, the final product being a nanogel particle. The method is quite general and has been tested on a number of hydrophilic polymers, including polyelectrolytes and thermosensitive macromolecules. Further developments include a possibility of independent control of the product size and weight, as well as to control the internal structure of nanogels. Mechanisms and kinetics of the reactions involved, as well as structural aspects are studied in parallel by experimental methods, as pulse radiolysis and laser light scattering, and by Monte-Carlo simulations using the Co-operative Motion Algorithm.

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WATER STRUCTURE AND INTERMOLECULAR INTERACTIONS IN POLYMER HYDROGELS

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Polymer hydrogels are one of the most strongly investigated recently hi-tech materials mainly because of their potential applicability in nano- (electronic, surface modification, synthesis of nanoparticles) as well as in biotechnology [1-2]. Up to now, the special attention was focused on the correlation between a structure of polymer network and the properties of a gel. However in many cases hydrogels contain more than 99,9 % of water and the role of water in properties of these materials cannot be overestimate. Very high water fraction is often a source of experimental difficulties for various techniques (high ionic conductivity in dielectric spectroscopy, very high absorbance in IR spectroscopy). Raman spectroscopy seems to be a perfect tool to study hydrogels. Firstly, Raman activity of OH stretching multi-mode band being relatively low compare to IR absorption and simultaneously the bands related to stretching vibrations of CH_x groups are commonly strong. As it was shown, successful analysis of structure of imbibed water and intermolecular interactions in hydrogels is possible even for low concentration of polymer [3]. Moreover both hydrophilic and hydrophobic water-polymer interactions may be with use of this technique seen.

To show the possible application of Raman spectroscopy in the field of investigation of water contain systems, simple model should be chosen. A poly (vinyl methyl ether) (PVME) seems to be a perfect model system for studies of an intermolecular interactions in polymer-water mixtures (solutions, hydrogels). Moreover, that aqueous solutions of this amphiphilic polymer exhibit lower critical solution temperature (LCST) playing a crucial role in medical and pharmaceutical applications (such as drug delivery systems, artificial attenuators, sensors). LCST manifested in a case of hydrogel in volume phase transition (VPT - water is rapidly pulled out from shrinking polymer network) is a result of instable balance between hydrophilic and hydrophobic interactions.

In this work changes of intermolecular interactions in PVME hydrogels differing in crosslinking degree were studied with use of Raman spectroscopy. Comparison of vibrational stretching modes of CH_x groups (polymer) and water allowed to construct the picture of supramolecular structure of such gels, and what is more important, highly probable scenario of its changes during various processes (deswelling, VFT).

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CELLULOSE NANOFIBERS – DIRECTIONS OF DEVELOPMENT

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The Department of Man-Made Fibers is carried out long term research programmes considering on the development of making of cellulose fibers by NMMO method. The research is partially focused on the solutions of base problems connected to the technology of the fibers and the increasing of the scale of production. A lots of efforts are also devoted on the development of the new generations of cellulose fibers.

One of the research directions is focused on the obtaining of modified cellulose fibers with the special properties. Usually the modification is achieved by the direct introduction of nanoadditives to the spinning dope. Base on the present experience the pilot plant for the production of the cellulose fibers with the special properties would be build.

Another very significant direction of the research is the development of the cellulose nanofibers production by mean of NMMO method. The research is focused not only on the solution of the base problems connected to the method but also the research is related to the increasing of the scale of the production of cellulose nanofibers. The cellulose nanofibers can be applied as a very effective material for medical purposes and as a technical materials.

BIO- AND NANO-TECHNOLOGY IN DEPARTMENT OF TEXTILE FINISHING – TUL

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Antibacterial and antifungal finishing of flat textiles as well as polymer dosimetry in radiotherapy are among research interests of our group. As concerns the former one, attempts have been made to work out methods of preparation of nano-size metallic particles (silver included) and stable aqueous nano-dispersions of antibacterial properties. These are usually characterized in order to gain knowledge on size and size distribution, stability and rheological properties by means DLS, UV-Vis, Zeta potential and viscosimetry measurements. The application studies requires further testing of the above substrates in terms of methods of textile finishing, such as padding-squeezing-drying, ordinary and digital printing. Furthermore, modified textiles are examined to assess durability and strength of the effect of antimicrobial finishing through multiple washing and microbiological tests. Currently, a few textile finishing methods are protected by patent applications [1-3].

On the subject of the polymer gel dosimetry, this is regarded as unique technique for high resolution, three-dimensional radiation dose distribution measurements in radiotherapy. The polymer gel dosimeters are inherent tools of the polymer gel dosimetry and they are based on vinyl monomers embedded in physical gel matrix. Broad range of monomers was selected and each of them was successfully combined with other components that are crucial to fulfill the requirements for gel dosimeters, such as possibility of dose distribution measurements for doses even below 1 Gy and up to a few hundreds of grays, sound stability of recorded dose distribution, soft-tissue mimicking, and high dose sensitivity. Under ionizing radiation monomers convert to crosslinked structures thus “recording” the absorbed dose distribution as a distribution of altered gel dosimeter physicochemical properties. The properties include relaxation rate ($R2 = 1/T2$) of the gel that can be measured by means of e.g. Magnetic Resonance Imaging (MRI) using optimized multi echo sequences. Notwithstanding the fact that polymer gel dosimetry has already been outstandingly applied in various radiotherapy techniques still elementary research plays an important role in understanding the polymer gel dosimeters phenomenon. There is also a room for further advancements in the area of data readout, scanning techniques and protocols or chemistry of polymer gel dosimeters [4]. As concern the latter one our group is particularly interested in new active components for the process of designing other polymer gel dosimeters of enhanced properties for specific irradiation methods in radiotherapy treatment. Selected polymer gel compositions are protected by patent applications [5-6].

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