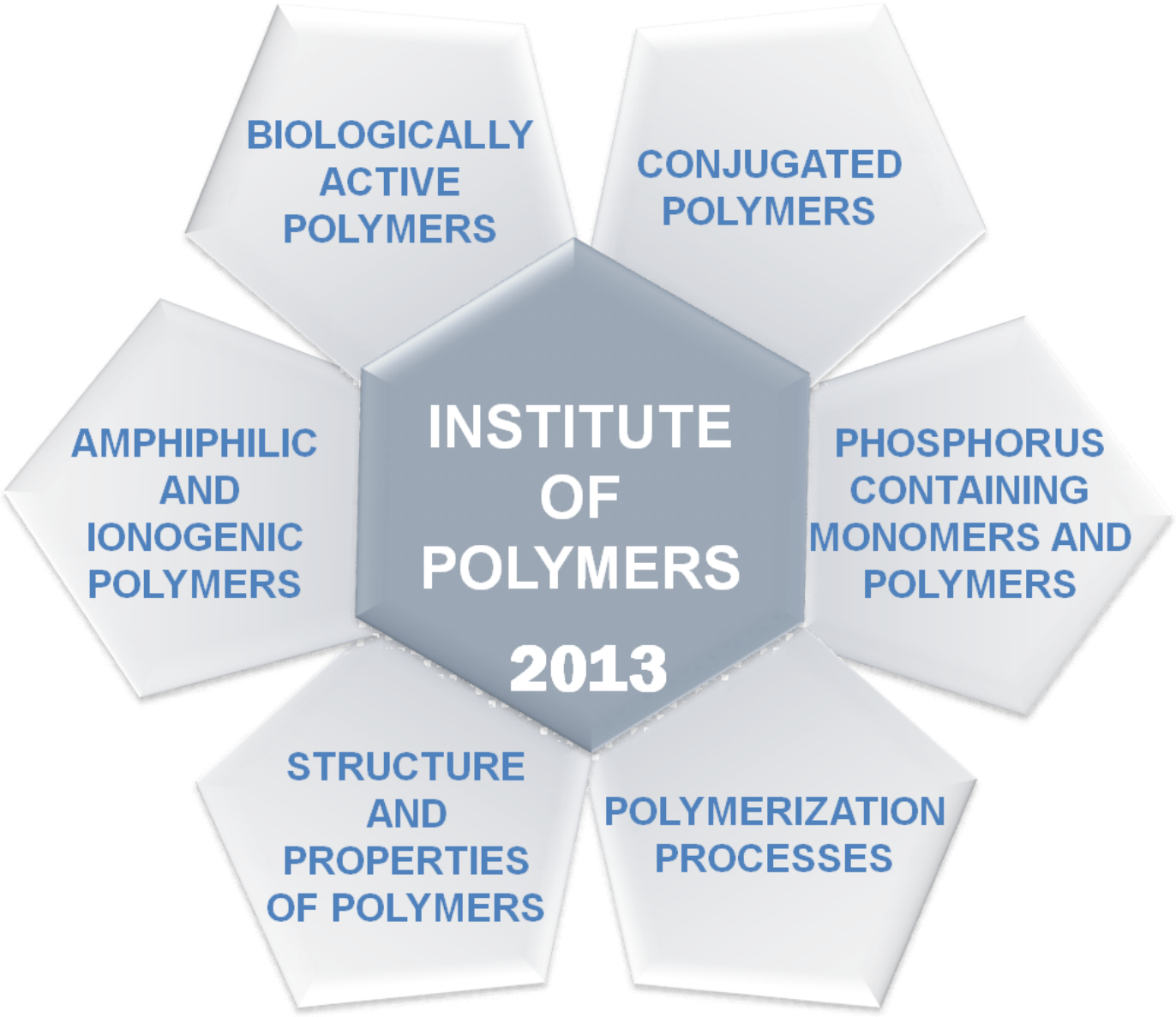
BULGARIAN ACADEMY OF SCIENCES



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This booklet aims to bring information to the academia, businesses and the general public about the research activities of the Institute of Polymers - BAS during year 2013. Briefly, the research areas, the most significant fundamental and applied studies, as well as the activities with national and public impact are presented. We expect that the dissemination of our activities will increase the possibility for further collaborations with new scientific and industrial partners.

The Institute of Polymers (IP-BAS) is an autonomous research unit belonging to the „Nanosciences, New Materials and Technologies Division" of the Bulgarian Academy of Sciences. IP is the country's leading center for research and innovation, PhD tuition and training in the field of polymer science. Since its founding in 1990, the Institute has strived for recognition as a center of excellence in the European Research Area.

The Institute accomplishes its mission - to do advanced research on polymers and polymer materials and to transform the generated knowledge into innovative materials, products, technologies and services in response to the needs of industry and society. The research at IP-BAS is organized on project basis and is being funded by budget as well as by grants from the National Science Fund (NSF), foreign research programmes and Framework Programmes of the European Commission. This approach guarantees that research is focused on problems relating to the public interests and priorities and the taxpayers funds are utilized effectively and transparently.

IP-BAS staff number 57 employees - 3 Full Professors, 12 Associate Professors, 14 Assistant Professors, PhD holders, 5 Research Assistants, 19 specialists with a MSc/MA degree and 4 specialists with high school diplomas, allocated in six research laboratories and administrative support unit. In 2013, 5 experience researchers, 1 intellectual property (IP) expert, 1 IP manager and 1 experienced technician were additionally hired within the framework of project POLINNOVA (http://polinnova.polymer.bas.bg/en/).

The research laboratories at IP-BAS have clearly defined thematic scopes with research objectives in compliance with the research strategy of the Institute. The coordination of the activities is assured through the Institute's annual research plan.

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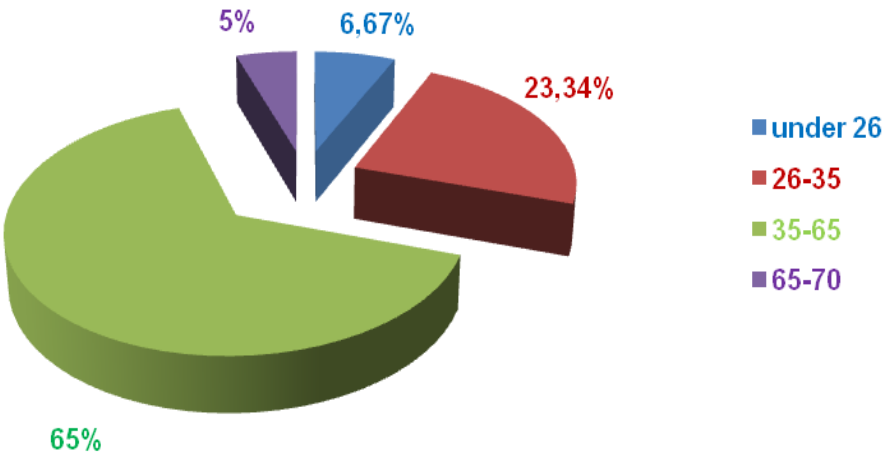
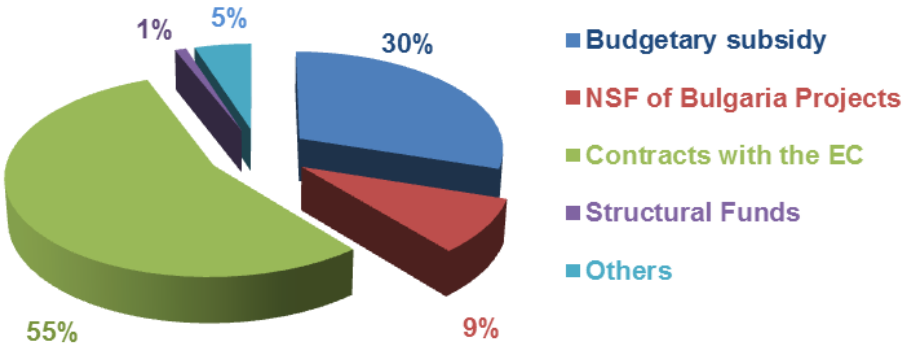
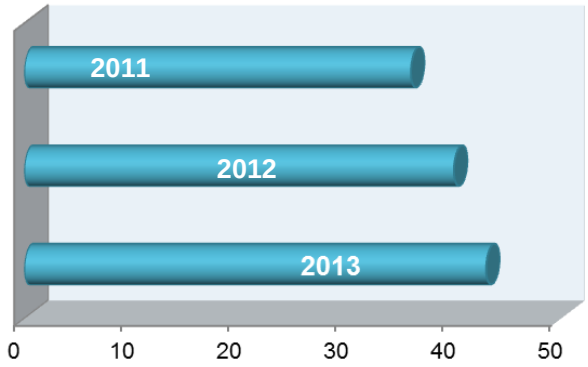
Age distribution of the staff



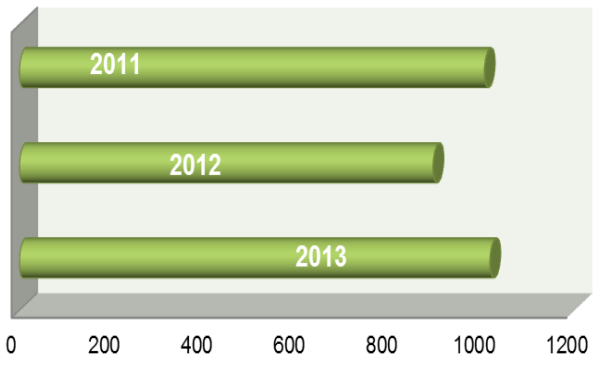
Budget 2011-2013
5 800 000 lv.



Number of scientific publications for the period 2011-2013



Number of citations for the perod 2011-2013



Laboratory **PHOSPHORUS CONTAINING MONOMERS AND POLYMERS**

HEAD: Assoc. Prof. Ivanka Kraicheva, PhD

Research Fields:

- Polymer-conjugates
- Phosphorus-containing amphiphilic polymers
- Polyphosphoesters with own biological activity
- Inorganic polymers and hybrid materials

Achievements in 2013:

Novel water soluble polymer complexes of Melphalan [*p*-bis(2-chloroethyl)amino-L-phenylalanine)], a bifunctional alkylating agent with cytotoxic activity,have been developed using polyphosphoesters as polymer carriers. The *in vitro* cytotoxic effect of the Melphalan formulations has been evaluated on three tumor cell lines (HuH7, SKBR3 and U87MG). (Bogomilova A, M. Hohn M, Gunther M, Troev K, Wagner E, Schreiner L *Polyphosphoester Conjugates and Complexes of Melphalan as Antitumoral Agents European* **Journal of Pharmaceutical Sciences** 2013, 50, 410-419).

A feasible PEGylation procedure for cisplatin nanocarrier was developed. It included synthesis of a PEGylating agent and the incorporation of cisplatin as a reversible linker for PEG modification of the star macromolecules. The PEGylation increased the stability of the nanocolloidal solution. The formation of PEG shell resulted in higher drug payload and improved drug release profile. The *in vitro* bioassay on human tumor cell lines confirmed that the PEGylated conjugates exhibited superior growth inhibitory activity compared to the nonPEGylated carrier. (Stoyanova E, Mitova V, Shestakova P, Kowalczuk A, Momekov G, Momekova D, Marcinkowski A, Koseva N *Reversibly PEGylated nanocarrier for cisplatin delivery* **Journal of Inorganic Biochemistry** 2013, 120, 54–62).

Novel polyphosphoesters, like poly(aminophosphonate)s and copolymers containing aminophosphonate and H-phosphonate units, have been synthesized. The copolymers have been evaluated for *in vitro* antitumor activity on a panel of seven human cancer cell lines. Safety testing *in vitro* and *in vivo* has been performed. The subcellular distribution of the substances in normal and tumor cells has been studied. (Kraicheva I, Vodenicharova E, Shenkov S, Tashev E, Tosheva T, Tsacheva I, Kril A, Topashka-Ancheva M, Georgieva A, Iliev I, Vladov I, Gerasimova T, Troev K *Synthesis, characterization, antitumor activity and safety testing of novel polyphosphoesters bearing anthracene-derived aminophosphonate units* **Bioorganic & Medicinal Chemistry** 2014, 22, 874-882)

The dinuclear platinum complex with a spermidine bridge was attached to polyphosphoesters. The conjugates exhibited profound cytotoxicity on five chemosensitive human tumor cell lines and one cisplatin-resistant model (HL-60/CDDP), and were found to induce apoptotic cell death. (MitovaV, Slavcheva S, Shestakova P, Momekova D, Stoyanov N, Momekov G, Troev K, Koseva N *Polyphosphoester conjugates of dinuclear platinum complex: Synthesis and evaluation of cytotoxic and the proapoptotic activity* **European Journal of Medicinal Chemistry** 2014, 72, 127-136).

Laboratory **STRUCTURE AND PROPERTIES OF POLYMERS**

HEAD: Assoc. Prof. Petar Petrov, DSc

Research Fields:

- Stimuli responsive polymer materials
- Photochemical crosslinking
- Polymer aggregates and nanoparticles
- Conjugated polymers
- Polymer modified carbon nanotubes
- Polymer-inorganic hybrid nanoparticles
- Polymer nanocomposites

Achievements in 2013:

Drug delivery systems based on novel block copolymer micelles have been developed. The advantages of micellar systems are their long-term stability and the ability for loading and prolonged release of poorly soluble in physiological media anticancer drugs. (Petrov PD, Yoncheva K, Mokreva P, Konstantinov S, Irache JM, Müller AHE *Poly(ethylene oxide)-block-poly(n-butyl acrylate)-block-poly(acrylic acid) triblock terpolymers with highly asymmetric hydrophilic blocks: Synthesis and aqueous solution properties* **Soft Matter** 2013, *9(36)*, 8745-8753)

pH sensitive super-macroporous cryogels from natural polymers 2-hydroxyethylcellulose and chitosan have been synthesized by photochemical crosslinking of frozen aqueous systems. Cryogels possess good mucoadhesive properties and can be exploited for preparation of drug delivery systems for treatment of vaginal infections. (Stoyneva V, Momekova D, Kostova B, Petrov P *Stimuli sensitive super-macroporous cryogels based on photo-crosslinked 2-hydroxyethylcellulose and chitosan* **Carbohydrate Polymers** 2014, *99*, 825-830)

The affinity of "Janus" micelles to adsorb on the surface of multi-walled carbon nanotubes in selective solvents has been discovered. The physical attachment of polymer micelles facilitates the dispersion of multi-walled carbon nanotubes in a variety of organic solvents and water at a very low micelle to nanotube mass ratio (1:10 w./w.). The modification method preserves the original structure of carbon nanotubes. (Gröschel AH, Löbling TI, Petrov PD, Müllner M, Kuttner C, Wieberger F, Müller AHE *Janus Micelles as effective supracolloidal dispersants for carbon nanotubes* **Angewandte Chemie - International Edition** 2013, *52(13),* 3602-3606)

Organic solar cells based on thin active layers from spin-coated aqueous dispersions of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) or solutions of poly(3-hexylthiophene) and [6.6]-phenyl-C_{61}-butyric acid methyl ester in chlorobenzene and 1,2-dichlorobenzene have been fabricated. (Sendova-Vassileva M, Bakardjieva V, Ivanova T, Lazarova E, Gancheva V, Tsocheva D, Mokreva P, Terlemezyan L, Vitanov P *Post-deposition treatment dependence of optical and structural properties of spin coated bulk heterojunction solar cells* **Comptes Rendus de L'Academie Bulgare des Sciences** 2013, *66(10)*, 1393-1398)

Laboratory **BIOLOGICALLY ACTIVE POLYMERS**
HEAD: Prof. Nevenka Manolova, DSc

Research Fields:

- Biodegradable and biocompatible polymers
- Bio-based polymer materials
- Fibrous materials by electrospinning and electrospaying
- Polymer materials for biomedical applications
- Bioactive nanohybrids
- Biohybrids for eco-safe agriculture

Achievements in 2013:

Novel hybrid nanofibrous materials of polymers from renewable sources (polyhydroxybutyrate and chitosan) containing nanoparticles of titanium dioxide and magnetite have been prepared. This has been achieved in an original way by combining nanotechnology approaches such as electrospinning and electrospraying. It has been shown that the new multifunctional materials are suitable for applications in regenerative medicine, in tissue engineering, and in solving environmental problems associated with water purification. (Korina E, Stoilova O, Manolova N, Rashkov I, **Macromolecular Bioscience,** 2013, *13*, 707-716; Korina E, Stoilova O, Manolova N, Rashkov I., **Journal of Materials Science**, 2014, *49*, 2144-2153).

Novel antibacterial materials from biocompatible synthetic polymers and the natural polymer chitosan have been developed. They have been obtained by applying easily feasible and original approaches based on the formation of polyelectrolyte complexes on the surface of electrospun nanomaterials. They are promising candidates for a variety of biomedical applications, (Kalinov K, Ignatova M, Maximova V, Rashkov I, Manolova N, **European Polymer Journal** 2014, *50*, 18-29).

For the first time the possibility to avoid detrimental interactions between drugs that may take place when preparing dual drug-loaded materials using the conventional techniques, has been revealed. To this aim, a particular electrospinning set-up has been proposed. (Toncheva A, Paneva D, Manolova N, Rashkov I, Mita L, Crispi S, Damiano GM, **Colloids&Surfaces A: Physicochemical and Engineering Aspects** 2013, *439*, 176–183).

New nanofibrous implants from polymers from renewable sources (polylactic acid and chitosan) and a natural compound with antitumor activity have been fabricated. They can be effectively used as systems for local treatment of solid tumors. (Ignatova M, Kalinov K, Manolova N, Toshkova R, Rashkov I, Alexandrov M, **Journal of Biomaterials Science, Polymer Edition**, 2014, *25*, 287-306).

Defect-free continuous polyimide nanofibers have been prepared (Peciulyte L, Rutkaite R, Zemaitaitis A, Ignatova M, Rashkov I, Manolova N, **Macromolecular Research** 2013, *21*, 419-426).

The most recent advances in the preparation of novel nanofibrous materials for wound dressing and wound healing, for systems for local cancer treatment, and in chitosan-based antibacterial materials by the electrospinning advanced technology have been summarized. (Ignatova M, Rashkov I, Manolova N, **Expert Opinion on Drug Delivery** 2013, *10*, 469-483 *feature article*; Ignatova M, Manolova N, Rashkov I, **Macromolecular Bioscience** 2013, *13*, 860-872), *invited review*.

Laboratory **Polymerization Processes**
HEAD: Prof. Stanislav Rangelov, DSc

Research fields

- Synthesis of well-defined polymers and copolymers via controlled polymerization techniques;
- Formation of polymeric and hybrid nanostructures via self-assembly and co-assembly;
- Advanced polymeric materials for pharmaceutical, biomedical, biotechnological, and ecological applications

Achievements:

Controlled polymerization techniques are employed to prepare a variety of amphiphilic copolymers of different chain architecture, topology, and functionality, which offer great potential in creating tailor-made supramolecular nanoparticles. A combination of experimental techniques is employed to obtain information about dimensions, structure, and dynamics of various systems in dilute solution. Polymeric and hybrid nanoparticles, prepared by self-assembly and co-assembly, have important pharmaceutical, medical, and analytical applications, in particular as vehicles for delivery of drugs, genes, diagnostic and therapeutic agents.

A series of poly(2-isopropyl-2-oxazoline)s of molecular weights ranging from 3600 to 8900 $g.mol^{-1}$ were prepared by cationic ring-opening polymerization from which stable nanosized colloidal particles (mesoglobules) were obtained. A thermosensitive cross-linked shell was constructed around the mesoglobules by seeded radical copolymerization of NIPAM and a cross-linking agent. The removal of the initial mesoglobules resulted in formation of hollow polymeric nanocapsules with a thermosensitive membrane. The nanocapsules reversibly change their dimensions during temperature variations below and above the transition of the membrane. (Toncheva, N.; Tsvetanov, Ch.; Rangelov, S.; Trzebicka, B.; Dworak, A. *Hydroxyl End-functionalized Poly(2-isopropyl oxazoline)s Used as Nano-sized Colloidal Templates for Preparation of Hollow Polymeric Nanocapsules.* ***Polymer*** *54(19)*, **2013**, 5166-73.)

Copolymers of different architecture containing thermally sensitive and polycationic blocks were synthesized and used to condense DNA into nanosized polyplexes. Both copolymers and their complexes with DNA exhibited low cytotoxicity. The polyplexes were further stabilized through formation of an outer shell via seeded radical polymerization of an acrylic monomer in the presence of a bio-reducible cross-linker. Finally, to provide some initial evidence for biological activity, the *in-vitro* transfection ability of both coated and uncoated polyplexes was evaluated in HEK 293 cells. The results are encouraging for future gene delivery applications of the thermally sensitive polyplexes combined with the strategy for their stabilization.(Ivanova, E.; Dimitrov, I.; Kozarova, R.; Turmanova, S.; Apostolova, M. *Thermally Sensitive Polypeptide-based Copolymer for DNA Complexation into Stable Nanosized Polyplexes.* ***J Nanopart Res*** *15(1)*, **2013**, 1358; Ivanova, E.; Ivanova, N.; Apostolova, M.; Turmanova, S.; Dimitrov, I. *Polymer Gene Delivery Vectors Encapsulated in Thermally Sensitive Bioreducible Shell* ***Bioorg Med Chem Lett*** *23(14)*, **2013**, 4080)

Polysulfones tethered with different types of sulfonated side groups were synthesized and investigated in a comparative study as proton exchange membrane (PEM) candidates. For the same purpose, a novel fluorinated monomer with pendant sulfonate group was synthesized and its controlled polymerization under aqueous ATRP conditions was demonstrated (Nielsen, M.; Dimitrov, I.; Takamuku, Sh.; Jankova, K.; Jannasch, P.; Hvilsted, S. *Dendronised Polymer Architectures for Fuel Cell Membranes.* ***Fuel Cells*** *13 (3),* **2013**, 342; Dimitrov, I.; Jankova, K.; Hvilsted, S. *Synthesis and ATRP of Novel Fluorinated Aromatic Monomer with Pendant Sulfonate Group* ***J Fluor Chem*** *149*, **2013**, 30-35).

Laboratory **CONJUGATED POLYMERS**

HEAD: Assoc. Prof. Vesselin Sinigersky, PhD

Research fields:

- Proton conducting polymer electrolytes
- Preparation of polybenzimidazole based membranes for fuel cells
- Nanocomposite membranes for fuel cells
- Polybenzimidazole fibers prepared by wet- and electrospinning
- Novel biodegradable polymer materials for food packaging
- Synthesis of electron conducting polymers via carbonyl-olefin exchange reaction

Achievements in 2013:

Low/middle-temperature membranes for fuel cells working up to 120°C based on polybenzimidazole (PBI), containing immobilized phosphonic and/or sulfonic acid groups or PBI, containing cross-linked PVPhA and/or PVSA were prepared. (V.Sinigersky, D. Budurova, H. Penchev, F. Ublekov, I., *Polybenzimidazole-graft-polyvinylphosphonic acid—proton conducting fuel cell membranes*, ***Journal of Applied Polymer Science*** *129 (3)*, **2013**, 1223-1231,; V. Sinigersky, H. Penchev, F. Ublekov, M. Staneva, D. Budurova, I. Radev, V. Peinecke, *Novel Middle Temperature PEM Fuel Cell Membranes – Polybenzimidazole Containing Immobilized Phosphoric – or Sulfonic Acid Groups*, ***Proceedings of EFC 2013****, Fifth European Fuel Cell&Application Conference – Piero Lunghi Conference*, p. 61-62, **2013**).

High temperature membranes for fuel cells working up to 180°C based on chemically cross-linked para-, meta- and AB-PBI, doped with PA with improved mechanical properties and proton conductivity (at some cases reaching 400 $mS.cm^{-1}$) and cross-linked para-PBI, doped with sulfuric acid (proton conductivity 647 $mS.cm^{-1}$) were developed.

Nanocomposite membranes based on PBI with incorporated inorganic fillers (montmorilonite, graphene oxide, carbon black) with improved mechanical properties and proton conductivity (above 400 $mS.cm^{-1}$) were prepared. (H. Penchev, M. Staneva, F. Ublekov, D. Budurova, V. Sinigersky, V. Geoorgiev, I. Radev, V. Peinecke, *Novel High Temperature PEM Fuel Cell Membranes – Composite AB-PBI/Carbon Black, Doped with Phosphoric Acid*, ***Proceedings of EFC 2013****, Fifth European Fuel Cell&Application Conference – Piero Lunghi Conference*, p. 59-60, **2013**).

Novel biodegradable polymer materials based on polylactic acid and polyhydroxyalkanoates suitable for food packaging applications were fabricated. For the preparation of this materials highly efficient technological processes e.g. reactive extrusion was used.

New method for the synthesis of R-substituted polyethynes bearing carbonyl or olefin end groups – methathesis of phenylalkines and an aldehyde catalyzed by nanosized ferite based catalyst ($NixFe_3$-xO_4) were studied. (S. Dimova, K. Zaharieva, Ch. Jossifov, Z. Cherkezova-Zheleva,I. Mitov, *Metathesis of Phenylalkylenes and Aldehyde by Nanodimensional Ferrite Catalyst,* ***Journal of Chemical Technology and Metallurgy***, *48(1)*, **2013**, 28-33).

Laboratory of

AMPHIPHILIC AND IONOGENIC POLYMERS

HEAD: Assoc. Prof. Darinka Christova, PhD

Research fields

- Amphiphilic copolymers and networks of controlled composition, structure and hydrophilic-hydrophobic balance
- Temperature and pH-responsive polymer materials for application in medicine, pharmacy and biotechnology
- Hybrid electroactive IPNs and hydrogels
- Composite polymer membranes with temperature controlled permeability

Achievements:

Current research activities comprise synthesis of well-defined amphiphilic and ionic/ionogenic polymers of controlled macromolecular structure and tailored properties using advanced polymerization methods and post-polymerization transformations, and investigation of their stimuli-responsive properties. The efforts are directed to the development of temperature- and pH-responsive copolymers of diverse macromolecular architecture (linear, branched, cross-linked) and intelligent materials that reversibly change their properties in response to the changes in environmental parameters.

The potential of temperature-sensitive amphiphilic copolymer networks based on polyoxazolines as effective carriers of drugs was studied. Two therapeutic agents of distinctive properties were considered as model drug molecules – ibuprofen, a hydrophobic analgesic with a very low solubility in aqueous media, and metoprolol tartrate, well water soluble beta-blocker. The release kinetics profiles of the drug loaded networks proved the feasibility of these materials as highly effective platforms for sustained drug delivery. Another drug delivery system was developed based on a series of cationic block copolymers and dexamethasone phosphate. Nanosized pH-responsive drug carriers of low cytotoxicity and high (up to 80%) drug loading capacity were obtained. The ability of these new drug carriers to regulate corticosteroid dexamethasone release for 24 hours was demonstrated *in vitro*.

Hybrid polymer networks and hydrogels of a variety of compositions and structure were synthesized and studied in view of potential biotechnological application. These include smart hydrogels for synthetic membranes with temperature-controlled permeability; biosorbent hydrogels based on PVA-immobilized biomass of filamentous fungi for remediation of heavy metal ions; electroactive copolymer hydrogels and composites for application as actuators and switches.

Most relevant publications:

[1] B. Kostova, K. Ivanova-Mileva, D. Rachev, D. Christova. *Study of the potential of amphiphilic conetworks based on poly(2-ethyl-2-oxazoline) as new platforms for delivery of drugs with limited solubility.* **AAPS PharmSciTech** 14 (2013) 352-359.

[2] D. Georgieva, B. Kostova, S. Ivanova, K. Balashev, D. Rachev, D. Christova. *pH-responsive drug delivery nanosystems based on star-shaped copolyelectrolytes.* **Nanoscience & Nanotechnology: 15th International workshop (NANO 2013)**. 21-23 November 2013, Sofia, Bulgaria.

[3] K. Tsekova, D. Christova, D. Todorova, S. Ivanova. *Removal of Cu(II), Co(II) and Fe(III) ions from ternary solution by free and entrapped in PVA-hydrogel biomass of Penicilium cyclopium.* **Biotechnology & Biotechnological Equipment** 25 (4 Suppl) (2011) 41-46.

[4] K. Tsekova, D. Christova, V. Dencheva, S. Ganeva. *Biosorption of binary mixture of copper and cobalt by free and immobilized biomass of Penicillium cyclopium.* **Compt. Rendu. Acad. Bulg. Sci.** 63 (2010) 85-90.

[5] D. Christova, R. Velichkova, S. Ivanova, K. Mileva. *Hydrophilic and amphiphilic polymer networks of varied architecture and hydrogels there from.* **Journal of Bulgarian Academy of Sciences** 2 (2010) 42-50.

Priority research fields

New polymer materials and technologies with potential application in medicine and pharmacy are the main fields of fundamental and applied research carried out at the Institute. The activities involved preparation of novel drug delivery systems with improved colloidal stability, activity, and other characteristics. In 2013, 8 projects related to the above mentioned topics were implemented by the staff of 5 laboratories with the financial support of the National Science Fund. In addition, the research activities of PhD students and early stage researchers were supported by project funded by OP "Human Resources Development".

The research of IP-BAS also deals with various aspects of environment protection which is a subject matter of the research plans of three laboratories. The main tasks are preparation of novel polymer materials from renewable resources: hybrid micro- and nanosized materials based on poly(lactic acid) and polyhydroxyalcanoates; cryogels based on cellulose derivatives, dextran and chitosan; recycling of polymers.

The preparation of polymer materials for alternative energy sources is the research field of two research groups at IP-BAS. Scientists from the Institute in cooperation with partners from BAS and abroad have contributed to the development of polymer membranes for fuel cells. In the last year 2 papers were published as a result of scientific cooperation with the Danish Technical University. In the course of 2013 the studies on the preparation of membrane-electrode packs for hydrogen generation via water hydrolysis and organic solar cells were also continued.

Research results achieved in 2013

The research results have been published in **40** articles, 31 of them appeared in specialized journals with impact factor, and **2** books. 35 % of those articles are in journals whose impact factor is higher than 2.5.

The top articles ranked according to the impact factor of the journals wherein they appeared are given below:

1. A.H., Gröschel, T.I. Löbling, P.D. Petrov, M. Müllner, C. Kuttner, F. Wieberger, A.H.E. Müller, *Janus Micelles as effective supracolloidal dispersants for carbon nanotubes*, ***Angewandte Chemie - International Edition***, 52, 2013, 3602-3606, ISSN: 1521-3773, IF^{2012} 13.734.

2. F.B. Madsen, I.V. Dimitrov, A. Daugaard, S. Hvilsted, A.L. Skov, *Novel cross-linkers for PDMS networks for controlled and well distributed grafting of functionalities by click chemistry*, ***Polymer Chemistry***, 4, 2013, 1700-1707, ISSN: 1759-9954, IF^{2012} 5.231.

3. M. Ignatova, I. Rashkov, N. Manolova, *Drug-loaded electrospun materials in wound-dressing applications and in local cancer treatment; invited review*, ***Expert Opinion on Drug Delivery***, 10, 2013, 469-483, 86, ISSN: 17425247, IF^{2012} 4.869.

4. P.D. Petrov, K. Yoncheva, P. Mokreva, S. Konstantinov, J.M. Irache, A.H.E. Müller, *Poly(ethylene oxide)-block-poly(n-butyl acrylate)-block-poly(acrylic*

acid) triblock terpolymers with highly asymmetric hydrophilic blocks: Synthesis and aqueous solution properties, ***Soft Matter***, 9, 2013, 8745-8753, ISSN 1744-6848, IF^{2012} 3.909.

5. M. Ignatova, N. Manolova, I. Rashkov, *Electrospun antibacterial chitosan-based fibers,* ***Macromolecular Bioscience***, 13, 2013, 860-872, 87, ISSN: 1616-5195, IF^{2012} 3.742.

6. E. Korina, O. Stoilova, N. Manolova, I. Rashkov, *Multifunctional hybrid materials from poly(3-hydroxybutyrate), TiO_2 nanoparticles, and chitosan oligomers by combining electrospinning/electrospraying and impregnation*, ***Macromolecular Bioscience***, 13, 2013, 707-716, ISSN: 1616-5195, IF^{2012} 3.742.

In the last year the scientists from IP-BAS co-authored two books:

1. S. Rangelov, S. Pispas, *Polymer and Polymer-Hybrid Nanoparticles: From Synthesis to Biomedical Applications*. 483 pages, CRC Press, Taylor & Francis Group. Boca Raton, FL. 2013, ISBN: 978-1-4398-6907-9.

2. P. D. Petrov, *Preparation of polymer and hybrid systems via photo-chemical processes*, Marin Drinov press, 2013, ISBN 978-954-322-640-5.

The communications presented at national and international scientific events are **66** of which 35 supported by POLINNOVA project. In particular, 16 scientists from IP-BAS attended European Polymer Congress 2013 held in Pisa, Italy.

282 papers by scientists from IP-BAS were cited **1018** in 2013 that sets a 3.61 average citation per article (3.34 for 2012).

In 2013, scientists from IP-BAS received the following awards:

- Corr. Member Iliya Rashkov and Corr. Member Christo Tsvetanov - honorary award of BAS "Marin Drinov" for significant scientific achievements;
- Dr. Emi Haladjova - UNESCO Award 2013 "For Women in Science";
- Dr. Georgi Georgiev - "Prof. Ivan Shopov" award for outstanding young scientist in the field of polymers.

Most important scientific achievement in 2013

Multifunctional hybrid materials based on polymers from renewable sources

Novel multifunctional hybrid materials based on polymers from renewable sources were prepared as promising scaffolds for the regenerative medicine and tissue engineering, as well as for use in water and air purification from organic pollutants. The design of the materials was tailored purposely by combining the advanced technologies of electrospinning and electrospraying. It was demonstrated that the embedded nanoparticles of TiO_2 and magnetite (Fe_3O_4) impart targeted properties of the materials and renders them suitable for specific applications having social and economic impact. Furthermore, the nanofibrous hybrid biomaterials preserved the photocatalytic activity of TiO_2 and magnetic properties of Fe_3O_4 embedded therein, and manifested a considerable biocidal effect against pathogenic bacteria (E. coli). They are compatible with human

mesenchymal stem cells and ensure a favorable environment for their development.

Most important applied research achievement in 2013

Nanosized antitumor systems

Drug delivery systems based on novel nano-sized polymeric carriers for improved activity of anticancer drugs have been developed. Polymeric carriers comprise a hydrophobic core and a double-hydrophilic shell. The anticancer drugs paclitaxel or cisplatin are incorporated into the micellar core, while the outer layer, composed of water soluble and biocompatible poly(ethylene oxide), provides good colloidal stability and prolonged circulation of nanoparticles in the blood stream. These properties, as well as the sustained release of the active substance, offer the possibility of improving the therapeutic index of the agent and increase the potential of the systems developed for clinical use. (Project leaders: Assoc. Prof. Neli Koseva and Assoc. Prof. Petar Petrov)

Innovation activities

The scientific priorities of IP-BAS and a significant part of the scientific team achievements possess an innovation potential. Various advanced methods are being developed to obtain new polymeric materials with target properties, which is key factor for creation of high technologies. It covers interdisciplinary research and development of scientific products with potential application in the following areas: medicine and pharmacy, ecology, agriculture, biotechnology and foods. Examples of scientific achievements are: nanosized systems, polymer hydrogels, micro- and nanofibrous materials as carriers of biologically active agents (DNA, antibacterial agents, antitumor drugs, etc.); developing of new polymers with a biological activity; biodegradable polymeric materials etc.

Researchers from IP-BAS are co-authors of 28 patents: 1 Bulgarian, 1 Japanese and 26 protected patents in European Patent Office and other countries such as USA, France, China, Canada and others. The patents with international participations are supported by foreign companies or organizations. An application for Bulgarian patent is in progress.

A three-day course on “Intellectual property rights” was carried out in July 2013 under a contract № 316 086 POLINNOVA. Its aim was to train the researchers from IP-BAS and to introduce them to the industrial property in its various types, procedures for submission of patent applications and useful models as well as to give guidelines about the technology transfer and commercialization of research products and technologies.

On 03/10/2013, during the annual International Fair Plovdiv, the expertise and achievements of IP-BAS were presented in front of different companies members of Bulgarian Association Polymers.

Tuition

In 2013, **12** PhD students were trained at the Institute, including one in extramural studies. In 2013, 3 new PhD students started their education at IP-

BAS. The scientists from IP-BAS are also co-supervisors of 3 PhD students from other academia.

Researchers from IP-BAS delivered lectures at the University of Orleans, France (Prof. N. Manolova, DSc) and Kinki University, Japan (Prof. K. Troev, DSc). There were also specialized lecture courses to students of the Physics Department at Sofia University "St. Kliment Ohridski" and Medical University, Sofia. Two graduate students defended their diploma thesis. Under the contract "Student Practice" OP-HRD at the Ministry of Education and the ESF in 2013 17 students held their practice in IP-BAS with various mentoring programs.

Within the Doctoral School at BAS two lecture courses were delivered. One of them, "Polymeric and polymer-hybrid nanoparticles - synthetic approaches, self-association and potential biomedical applications," with speakers Dr. Iv. Dimitrov and Prof. St. Rangelov, was launched in 2013.

Two theses for earning the scientific degree "Doctor of Science" were defended in 2013:

- Assoc. Prof. Vladimir Baranovsky - "Interpolymer complexes based on hydrogen bonds"
- Assoc. Prof. Petar Petrov - "Preparation of polymer and hybrid systems by photochemical processes".

A thesis for conferring on educational and scientific degree "Doctor" was defended by Antonia Tontcheva on the topic "Electrospinning of polylactides and ionizable biologically active substances for preparation of novel microfibrous materials".

Two Assistant Professors - Dr. Philip Ublekov and Dr. Antonia Tontcheva were selected through competitions by the Scientific Council of IP-BAS during the past year.

Societal impact of the research activities

Polymer science helps to meet the needs of society for new materials, processes and services as well as in its daily needs and also in solving global issues such as pollution of the environment, efficient use of natural resources and others. Polymeric materials contribute to the progress in many fields such as medicine, transportation, information and communication technologies, etc. Scientists from IP-BAS have prepared novel polymer carriers of biologically active substances (antibiotics, anticancer drugs, DNA, etc.), new polymers with intrinsic biological activity, radioprotective polymeric materials, high-temperature fuel cell membranes, etc.

The tuition of graduate students and specialists in the field of polymers is an integral part of the scientist's activity in IP-BAS. This ensures the growth of highly qualified professionals and researchers as well as establishes conditions for development of polymer science in the country. In addition, the updating of analytical and specialized equipment allows expansion of our contacts with the industry, the performance of specific analyzes and consultations, and also participation in research and innovation projects.

Cooperation with institutions

During the reporting period, IP-BAS continues the traditional intensive cooperation with various universities and research institutes as well as with the following institutions:

- NPP Kozloduy Ltd. under the Memorandum for joint scientific and technical projects;
- Bulgarian Association Polymers, involving 37 Bulgarian companies in the field of processing of polymers. There is a signed Memorandum for cooperation in developing expert opinion and joint actions to increase the innovation potential of the Bulgarian polymer science and for sustainable development of Bulgarian polymer industry. Bulgarian Association Polymers is also a partner of IP-BAS in project POLINNOVA, funded by EC under the Seventh Framework Program.

National and operative activities

In 2013, researchers from IP-BAS have developed expert opinions and expertise concerning: The use of carbon dioxide; Determination of end-of-waste criteria; Technical and chemical expert reports in litigation in the District Court - Varna and Administrative Court – Varna.

Scientists from IP-BAS were involved in national and international expert committees such as: Programme Committee of "Marie Skłodowska-Curie actions " under Horizon 2020; Domain Committee - Domain “Chemistry and Molecular Sciences and Technologies” of COST; Management Committee of COST action CM1302; National network for coordination and implementation of Nanotechnology activities, advanced materials, manufacturing and processing of the EU Framework Program for Research and Innovation, "Horizon 2020" (2014-2020), National Committee of the International Union of Pure and Applied Chemistry (IUPAC); National representatives of polymer division of IUPAC, Standing Committee on Natural sciences at NSF, National Council for innovation at MEET.

Scientists from IP-BAS have prepared reviews for a research project of the National Research Fund of Switzerland, 4 proposals for competitions OS 2013-1 and OS 2013-2 COST program, project applications of Bulgarian NSF and the Medical University - Plovdiv. Researchers from IP-BAS have referred theses for academic degrees and have delivered opinions for academic promotions as follows: - 8 reviews and 1 opinion for "Doctor" degree, 3 reviews and 2 opinions for "Doctor of Science" degree.

IP-BAS has been established as center for discussions and spreading of expert knowledge in the field of polymers and polymer materials. The Institute’s colloquium POLYMERS chaired by Assoc. Prof. Ivaylo Dimitrov has been a forum where the prominent scientists from the country and abroad present their achievements and the latest trends in polymer science. The list of international lecturers at the colloquium in 2013 is given below:

- Prof. Axel Müller, Mainz University „Johannes Gutenberg” –Germany;

- Prof. Jacek Stawinski, Institute of Bioorganic Chemistry, Polish Academy of Sciences;
- Prof. Alexander Wasserman, Institute of Chemical Physics „N.N. Nemnov", Russian Academy of Sciences;
- Prof. Geoffrey Mitchell, Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, Portugal.

International cooperation

The researchers from IP-BAS have been fostering a long-lasting scientific contacts with their colleagues from European and Asian academia. The research is carried out within the frames of projects both on academic and institute level. Researchers from IP-BAS have implemented 9 projects within the bilateral agreements for scientific cooperation of the Bulgarian Academy of Sciences: 3 with the Centre for Polymer and Carbon Materials - Polish Academy of Sciences, 2 with the Russian Academy of Sciences (Institute of Physical Chemistry and Institute of Macromolecular Compounds), 1 with CNRS (Institute of Chemistry and Materials Science, France), 1 with WBI/FRS-FNRS (University of Mons, Belgium), 1 with the Institute of Polymers - Slovak Academy of Sciences and 1 with Arabic Republic of Egypt.

In 2013, according to the rotation principle, the Central and Eastern European Polymer Network (CEEPN) was chaired by IP-BAS. The network unites polymer research institutes of eight countries from Central and Eastern Europe. On 27.09.2013, IP-BAS hosted the IX Annual Meeting of the Board of the national representatives of the Central and Eastern European Polymer Network. The workshop was attended by: Prof. Dr. M. Kowalchuk (General Secretary of the Central and Eastern polymer network), Dr. F. Rypachek (Czech Republic), Prof. Dr. A. Dworak and Prof. Dr. M. Basco (Poland), Prof. Dr. B. Simioniescu (Romania), Prof. Dr. Igor Lachik (Slovakia), Prof. Dr. M. Zigon (Slovenia) Assoc. Prof. N. Koseva (national representative for Bulgaria and President of Central and Eastern Polymer Network for 2013).

Within the frames of contract No 316 086 POLINNOVA, an international workshop on "Polymer Materials - Research and Innovation" was held in "Belchin Garden" hotel, Belchin Banya, on 30.10-01.11.2013. During the meeting reports were presented by foreign partners of the project as well as by researchers from IP-BAS. Particular attention was paid on Intellectual property rights.

IP-BAS was visited by 27 foreign scientists from Poland, Russia, Greece, Belgium, France, Egypt, Turkey, Portugal, Sweden, Slovakia, Romania, Slovenia, Spain, UK and the Czech Republic within the bilateral agreement for scientific cooperation (EBR), project of institutional agreement (contract No 316086 POLINNOVA) or external funding.

The research carried out within the frames of projects concerns the national and European priority fields such as energy saving, renewable resources and improving the quality of life. The international cooperation favors the mobility and exchange of researchers. The collaborations with international teams enhance the competitiveness and stimulates the innovation activities of the scientists from IP-

BAS. 30% of our articles published in 2013 are in co-authorship with our partners from abroad.

In 2013, IP-BAS participated in the following polymer networks: European Scientific Network for artificial muscles, Precision Polymer Materials of the European Science Foundation; „Electrospun Nano-Fibres for Bio Inspired Composite Materials and Innovative Industrial Applications", COPOLYMAT- between IP-BAS and the Centre for Polymer and Carbon Materials, Polish Academy of Sciences and European Phosphorus Sciences Network (PhoSciNet).

Important projects

IP-BAS is implementing the project **Strengthening the Research Capacity and Innovation Potential of the Institute of Polymers at the Bulgarian Academy of Sciences for Further Integration into the Era (POLINNOVA)**, Grant No 316086. The project is funded under the FP7 Capacities Program, Research Potential. The funding estimates 4 207 698 BGN.

Within the frames of POLINNOVA project in 2013 IP-BAS purchased and installed a new GPC line for precise determination of molar mass characteristics of polymers and polymer materials in solution, equipped with set of detectors: RI, UV and MALLS.

Scientist from IP-BAS realized long term research stays at the partnering organizations: two at the University of Mons, two at the Centre for Polymer and Carbon Materials, PAN, one at the University of Ghent and one at the University of Castilla La Mancha. The short term research stays were two: at the Centre for Polymer and Carbon Materials, PAN and University of Mons. Leading European researchers from the partnering organizations who visited IP-BAS were from the Centre for Polymer and Carbon Materials, PAN, University of Castilla La Mancha and Institute of Theoretical and Physical Chemistry, Greek National Scientific Research Foundation.

POLINNOVA project allowed for increasing the human potential of IP-BAS by recruiting five experienced scientists with expertise in the field of polymers and polymeric materials, two experts on intellectual property and an experienced technician. In addition, the project stimulates the search for partnership with targeted industrial representatives.

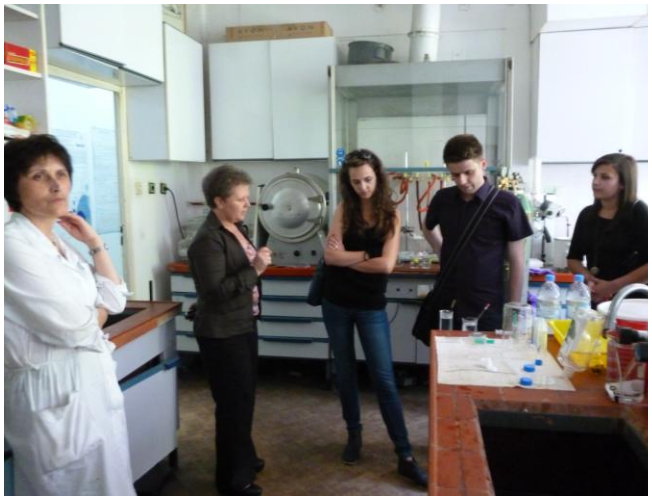
In 2013 the applications for another two important projects were approved:

- BG051PO001-3.3.06-0017 **Development of the scientific potential for sustainable career development of young scientists, PhD students and post-docs in the priority areas of polymer science**, OP "Human Resources Development" Fund : 269 406.93 BGN.
- BG161PO003-1.2.04-0096-C0001, **Support for applied research at the Institute of Polymers for development of new polymeric and composite materials from unconventional raw material sources with applications in environmental, energy and health technologies**, OP "Development of the Competitiveness of the Bulgarian Economy" 2007-2013, Fund: 2 395 365.00 BGN.

„Open doors day" at IP-BAS, May 22nd, 2013








Within this event the Institute was visited by students and professors from the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski", the University of Chemical Technology and Metallurgy – Sofia, the Faculty of Pharmacy at the Medical University – Sofia, our colleagues from Institutes at the Bulgarian Academy of Sciences and students from the National High School of Mathematics and Science "Acad. Lubomir Chakalov "- Sofia.

IVth poster session “Young scientists in the world of polymers”, June 6th, 2013 г.

This event was organized by a team of young researchers from IP-BAS with the financial support of project POLINNOVA. 28 PhD students, post-docs and young researchers from the leading universities and institutions caring out research oriented to polymer science in Bulgaria presented their results. An award for the best poster presentation was given to Mrs. H. Grancharova from the Faculty of Chemistry and Pharmacy at Sofia University “St. Kliment Ohridski”






STIMULI RESPONSIVE POLYMERS
AND POLYMER MATERIALS
Andrzej Dworak