

DAY 1

Scientific Tracks & Abstracts



3rd Edition of International Conference and Exhibition on

Polymer Chemistry

March 26-28, 2018 | Vienna, Austria

DAY 1

March 26, 2018

Sessions

Polymer Nanotechnology

Session Chair
Gerhard Eder

Johannes Kepler University, Austria

Session Co-chair
Andreas Taubert

University of Potsdam, Germany

Session Introduction

Title: Silver nanowires as a platform for plasmon engineering

Joanna Niedziółka- Jönsson, Institute of Physical Chemistry, Polish Academy of Sciences, Poland

Title: Plastic Scintillator, exploration of photo-physical properties and chemical optimisation

BERTRAND Guillaume, CEA Saclay, France

Title: SnO₂ nanoparticles: Their structural, electrical and optical properties

Vinita Sharma, BBD Government College, India

Title: Synthesis of nanochitosan Bombyx mori and its derivatives for medicine

Milusheva R.Yu, Institute of Polymer Chemistry and Physics Academy of Sciences of Uzbekistan, Uzbekistan

Title: Carbon and graphite filler composites of ethylene-octene copolymer – potential candidates for pressure/strain sensors

Rajesh Theravalappil, King Fahd University of Petroleum and Minerals, Saudi Arabia

Title: Fabrication of CNT-based conducting polymer nanocomposites and their applications in direct methanol fuel cells

You-Jun Fan, Guangxi Normal University, China

Title: Photo-design of metal polymer nanomaterials and nanostructures

Lavinia Balan, CNRS Institut de Science des Matériaux de Mulhouse, France

Title: Exhibitor talk

Gundula Reitenbach, Physical Electronics GmbH, Germany

EuroSciCon



Polymer Chemistry 2018

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Joanna Niedziółka-Jönsson et al., Polym Sci, Volume 4
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SILVER NANOWIRES AS A PLATFORM FOR PLASMON ENGINEERING

¹Joanna Niedziółka-Jönsson and ²Sebastian Maćkowski

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Metallic nanowires, due to their plasmonic character combined with the ability to efficiently transport excitations, are highly suitable for controlling the optical properties of other nanostructures, such as polymers, nanocrystals or biomolecules. Importantly, while diameters of such nanowires, in the range of 100 nm, are small enough to exhibit plasmonic effects in the broad spectral range, their lengths exceeding tens of micrometers make them visible using standard microscopy. In addition, by functionalizing their surface, it is possible to tailor their biochemical function, for instance as sensors. In the talk, we will discuss selected experiments carried out using silver nanowires as building blocks of hybrid nanostructures. The first result was obtained by attaching photosynthetic pigment-protein complexes to the nanowires, where we demonstrate strong enhancement of fluorescence of these complexes due to plasmonic interactions. Additional effects associated with controlled geometry of this assembly will be discussed. Next, we describe the application of silver nanowires for enhancing absorption of organic polymers and macromolecular systems used in organic electronics. In this case, optical spectroscopy allows elucidating the processes responsible for the observed effects and enables for further optimization of actual devices. The final part of the presentation will focus on applying silver nanowires as a sensing platform for various species. Particular emphasis will be placed on methods of spatial positioning of such nanowires in a controlled manner on the surface, as this seems to be the key for any possible application.

Recent Publications:

1. T Klemens, A Świtlicka-Olszewska, B Machura, M Grucela, E Schab-Balcerzak, *et al.* (2016) Rhenium(I) terpyridine complexes – synthesis, photophysical properties and application in organic light emitting devices. *Dalton Transactions* 45:1746–1762.
2. P Kannan, M Los, J M Los and J Niedziolka-Jonsson (2014) T7 bacteriophage induced change of gold nanoparticle morphology: Biopolymer capped gold nanoparticles as a versatile probe for sensitive plasmonic biosensor. *Analyst* 139:3563–3571.

3. M Twardowska, I Kamińska, K Wiwatowski, K U Ashraf, R J Cogdell, *et al.* (2014) Fluorescence enhancement of photosynthetic complexes separated from nanoparticles by reduced graphene oxide layer. *Applied Physics Letters* 104:093–103.
4. K Smolarek, B Ebenhoch, N Czechowski, A Prymaczek, M Twardowska, *et al.* (2013) Silver nanowires enhance absorption of poly(3-hexylthiophene). *Applied Physics Letters* 103(203302):1–4.
5. M Olejnik, B Krajnik, D Kowalska, M Twardowska, N Czechowski, *et al.* (2013) Imaging of fluorescence enhancement in photosynthetic complexes coupled to silver nanowires. *Applied Physics Letters* 102(083703):1–5

Biography

Joanna Niedziółka-Jönsson is a professor at the Institute of Physical Chemistry Polish Academy of Sciences in Warsaw, Poland. She received PhD degree in chemistry in 2006 and habilitation in physical chemistry in 2015. Her research group focuses on surface modification of various substrates in the context of applying plasmonic nanostructures for sensing and optoelectronics. She is a co-author of 77 publications cited over 1100 times. Her Hirsch index is equal to 20. Presently she leads two research projects funded by the National Science Centre Poland.

Sebastian Mackowski is a professor of Physics in the Institute of Physics Nicolaus Copernicus University in Torun, Poland, as well as president of the Baltic Institute of Technology in Gdynia, Poland. He obtained PhD degree in 2003, habilitation in 2008, and the title of professor in 2016. He authored over 170 papers in international journals.

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Bertrand Guillaume, Polym Sci, Volume 4
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PLASTIC SCINTILLATOR, EXPLORATION OF PHOTO-PHYSICAL PROPERTIES AND CHEMICAL OPTIMISATION

Bertrand Guillaume

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Thanks to a good ratio between cost and performances, plastic scintillators are now in the center of radiation detection applications. But due to the fact that most of the formulations were created in the 50's, there is now a huge incentive in creating new recipes, due to increasing need of large scale detectors. The conversion of high energy ionisation to a visible photons emission is called scintillation. This process implies charge and exciton transport inside the bulk of the plastic. Different input ionisation (alpha, beta, gamma and neutron) give different ionisation trace and can lead to slight modification of the emission characteristics; hence leading to identification of the ionising particle. We are presenting here a comprehensive model of gamma and neutron interaction in plastic scintillators and the photophysical mechanism associated with gamma/neutron discrimination, with a particular emphasis on excited triplet state diffusion and recombination inside amorphous polystyrene matrices. More than the model, several chemical modifications of the polymer matrix as well as additives can enhance different scintillation properties. More particularly, addition of metal additives, high concentration of fluorophores, modification of the polymeric matrices and addition of cross-linking agents are essential for specializing the plastic towards a particular application. Here, again understanding charge and exciton transfers are central to optimize formulation. One of the main examples is the choices of heavy metal additives for enhancing properties. We will present here, our work on organometallic insertion inside plastic matrices and optimization of the formulation towards better scintillation properties.

Biography

Bertrand Guillaume is a Researcher at CEA Saclay near Paris, in France. He is an Organic Chemist and likes to apply chemical designs to materials science and more particularly light/matter interaction. His areas of research of interest include photovoltaic, organometallic and inorganic chemistry and porous materials. He is now specializing in design and optimization of plastic scintillator for nuclear instrumentation. His research interests include polymer chemistry, plastic scintillator, photophysics and organometallics.

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SnO₂ NANOPARTICLES: THEIR STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES

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Thin films or nanocrystalline particles of metal-oxide materials are an important class of inorganic polymers. Nanotechnology, by which these materials are being synthesized is an active area of current research activities in various fields, including energy production, medicines, electronics etc. In a span of past few decades nanomaterials have attracted a great research interest due to their unique properties and novel potential applications. Out of these, non-stoichiometric SnO₂ nanoparticles form an important class of materials which is a wide gap (3.64 eV), transparent in visible and NIR region, n-type semiconductor. It has a wide range of applications in the field of optics, electronics and catalysis. Oxide or mixed metal oxide nanomaterials of tin are an important class of materials because of their tunable physico-chemical properties. On the other hand, they have high chemical and mechanical strength. These materials have wide spread applications as gas sensors, transparent conducting electrodes e.g. solar cells, optoelectronic devices and as a catalyst for oxidation of solids. Structural features of the SnO₂ lattice can be controlled using various dopants in suitable concentrations and hence its optical and electrical properties can also be controlled accordingly. Many synthetic routes have been developed for the preparation of SnO₂ nanoparticle or films such as MOCVD, spray pyrolysis, hydrothermal route, sputtering of oxides and sol-gel technology. Out of these methods sol-gel technology (that involves a series of hydrolysis and polymerization reactions) is simple to perform by which homogeneity in composition as well as in morphology of nanoparticles could be achieved with high purity at comparatively low temperatures. This low temperature condition allows deposition of thin films of oxides at soft surfaces. Our previous studies on Sol-gel technology using metallorganic derivatives as single source molecular

precursors and also by others are in good agreement with this. In this report some structural, electrical and optical aspects of these materials (pure and doped) will be discussed in detail and will be compared with the results obtained from the studies on the sol-gel synthesis of mixed metal oxide (xSnO₂, SrO) nanoparticles of SnO₂ with SrO in basic medium. Results from XRD, SEM, TEM and electron diffraction patterns have shown the structural features of these SnO₂ nanoparticles. Electrical properties have been discussed with respect to carrier concentration and carrier mobility that ultimately effects the conductance in these materials. Particle size also play an important role. Optical properties are determined by direct energy band gap between conduction and valence band. Results from UV-vis spectroscopy (absorption, reflectance and transmittance) show the actual band gap in these materials. Direct measurement of the band gap (E_g) from the intercept of the energy axis in Tauc Plots, show its dependence on the type of dopant and its concentration and also on particle size.

Biography

Dr. Vinita Sharma is Associate Professor in Chemistry at Department of Higher Education, State Government of Rajasthan, India, Received M.Sc., Ph.D. in 2003 from University of Rajasthan, Jaipur, also carried out some research work at Bhabha Atomic Research Center-Mumbai, Post doctorate (2004-2007) from University of Rajasthan, Jaipur, working with present employer since last 15 years. Published 15 papers and 3 review articles in the field of metallorganic derivatives and materials Chemistry in the Journals of international repute and presented around 16 papers in various international/national seminars/conferences. Delivered 5 invited talks in conferences. Meanwhile received Research Award from UGC New Delhi of Central Government and Young Scientist award from Indian Chemical Society.

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SYNTHESIS OF NANOCHITOSAN BOMBYX MORI AND ITS DERIVATIVES FOR MEDICINE

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One of the leading positions in the list of industrially significant natural polymers, both in sense terms of availability and in the breadth of possible fields of application, for many years retains amino polysaccharide chitosan. Despite the fact that the unique characteristics of native chitosan ensure its relevance in various technological processes, chemical modification allows obtaining new products for solving specific problems. In this study, the synthesis of nano-chitosan Bombyx mori was carried out by fractional precipitation in the presence of a surface modifier. The optimal concentration of the solution of chitosan, pH, the ratio of the chitosan solution to stabilizer were determined experimentally. The resulting nano-chitosan had a low molecular weight of 70 kDa, an intrinsic viscosity of 1.5 dl/g, a nitrogen content of 8.22%, and a high solubility- 99.2%. Nano-chitosan Bombyx mori was tested for antibacterial activity on various strains of microorganisms: *St.saprofiticus*, *Str.pyogens*, *Ent.faecalis*, *Esch. Coli LP*, *Esch. Coli LN*, *Prot.vulgaris*, *Klebsiella*, *Actinomyces*. Investigations of the immunomodulatory properties of nanochitosan have been carried out and it has been revealed that the polymers have the ability to increase the immune response to erythrocytes of the mice, the antibody titer in the peripheral blood, stimulate cell proliferation in the central (thymus, bone marrow) and peripheral (spleen, lymph nodes) immunity organs, increase the number of erythrocytes and leukocytes in the blood of mice. When studying the effect of chitosan on the number of cells in the central organ of immunity-bone marrow, it was shown that chitosan, almost doubles the number of cells in the bone marrow. Initial chitosan has an obstacle to biomedical applications due to poor water solubility, a high positive charge in acidic media (pH <6.5), which induces, in contact with blood, problems such as hemolysis or thrombolysis. To overcome these problems, chitosan is chemically modified by grafting polyethylene glycol (PEG) to the chitosan chain. PEGylation of chitosan is mainly achieved by grafting PEG onto amino groups (N-modification), but this approach induces changes in the

chain of chitosan and the loss of physicochemical properties. PEGylation to OH-groups (O-modification) is more interesting, since the O-modification does not affect the free amino groups in the chitosan chain. Grafting of PEG on chitosan Bombyx mori was carried out in a sequence of several steps: activation of PEG monomethyl ether using triphenyl phosphate to prevent product hydrolysis, protecting the amino groups of chitosan with phthalic anhydride, reaction of N-phthaloyl chitosan and activated polyethylene glycol, removal of N-phthaloyl groups by hydrazine monohydrate. The graft copolymers of (PEG-O-ChsBm) with different content of amino groups were synthesized and nanoparticles of copolymers were obtained by self-organization in dilute aqueous solutions. The supramolecular assemblies of PEG-O-ChsBm copolymers were characterized by light scattering, a combination of TEM, SEM, and cryo-TEM. Nanoparticles with an average diameter in the range of 140 nm-210 nm, depending on the content of amino groups was obtained. The toxicity of the nanoparticles was evaluated in HeLa and THP-1 cell lines. It was show the nontoxicity of both the chitosan Bombyx mori and its nanoparticles, besides it was found that the content of amino groups in the nanoparticles of the PEG-O-ChsBm copolymers acts as a trigger for the delivery of molecules, including most effective way.

Biography

Milusheva R Yu is a leading researcher in the Institute of Polymer Chemistry and Physics Academy of Sciences of Uzbekistan. She awarded PhD from Tashkent Polytechnic Institute. Her research interests lies in chemistry of macromolecular compounds; chemistry and technology of chitin and its derivatives, the creation of nanostructured polymers; physicochemical properties and structural morphology of nanopolysaccharide systems. In the field of applied research - the development of preparations based on polysaccharides and their use in the treatment of diseases of various etiologies.

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Rajesh Theravalappil, Polym Sci, Volume 4
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CARBON AND GRAPHITE FILLER COMPOSITES OF ETHYLENE-OCTENE COPOLYMER: POTENTIAL CANDIDATES FOR PRESSURE/STRAIN SENSORS

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¹King Fahd University of Petroleum and Minerals, Saudi Arabia

²Tomas Bata University in Zlín, Czech Republic

Ethylene-octene copolymer (EOC) is a copolymer which exhibits low density, good elasticity and improved processability and widely being used in the automotive, electrical cable insulation and footwear applications. Conducting polymer composites of EOC (with octene content of 45 wt.%) were prepared using three different types of fillers; expandable graphite (EG), multiwall carbon nanotube (MWCNT) and carbon fiber (CF). EOC/EG composites were prepared by melt blending of EOC and EG, while EOC/MWCNT and EOC/CF composites were prepared by ultrasonication of EOC solutions/filler systems followed by precipitation. Electrical (both AC and DC) and thermal conductivities of composites were measured. Flammability resistance tests of the EOC/EG composites only were carried out and showed that expandable graphite is an excellent flame-retardant filler. Percolation behaviour of EOC/EG composites were observed at around 16 vol.% of filler loading while for EOC/CF it was at, 2.21 vol.% and for EOC/MWCNT, it was at 5.32 vol.% which is a clear indication of effect of filler, or aspect ratio of fillers in the composites. Stress at break and elongation at break of EOC/MWCNT and EOC/CF composites found increasing initially and

followed a downward trend which is mainly due to reduction in chain flexibility which predominates over the reinforcing effect of fillers. From shore-A hardness values, it is clear that even the highest filler level did not reduce the softness of composites. Good electrical/thermal conductivities and improved mechanical properties along with comparable shore-A hardness values of EOC composites with excellent residual strain (ϵ_r) of pure EOC which is a direct measure of elasticity of a material, shows the potential of EOC to find its application as strain sensors.

Biography

Rajesh Theravalappil obtained his PhD Degree in Chemistry and Materials Technology from Tomas Bata University in Zlín, Czech Republic in 2012. He joined the Center for Refining and Petrochemicals of the Research Institute, King Fahd University Petroleum and Minerals, Saudi Arabia post completion of his PhD and is currently a Research Scientist. He has 15 years of research and industrial experience in the field of polymer science. His research interest includes: polymer synthesis and characterization, petrochemicals, polymer blends and composites, material development.

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You-Jun Fan, Polym Sci, Volume 4
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FABRICATION OF CNT-BASED CONDUCTING POLYMER NANOCOMPOSITES AND THEIR APPLICATIONS IN DIRECT METHANOL FUEL CELLS

You-Jun Fan

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Carbon nanotubes (CNTs) have attracted great interest as catalyst supports due to their unique properties, including excellent electronic conductivity, large surface area and high chemical stability. However, pristine CNTs are chemically inert and can't readily disperse in organic solvents or aqueous solutions, which would be disadvantageous for the assembly and dispersion of catalytic nanoparticles. It is necessary to functionalize CNTs in order to improve their surface properties and dispersions in solvents. We have reported the functionalization of CNTs with conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polyindole (PIn) and used these nanocomposites as the support materials of Pt nanoparticles. It is found that the conducting polymer functionalization of CNTs not only remarkably enhanced the solubility of CNTs but also introduced homogeneous surface functional groups on the CNT surface. The conducting polymer functionalized CNTs supported Pt nanocatalysts, exhibit much higher electrocatalytic activity and stability than the Pt/CNTs and commercial Pt/C catalysts for methanol oxidation. Moreover, we have developed a novel strategy for the synthesis of sulfur-doped or sulphur and nitrogen co-doped CNTs as the highly efficient Pt-based catalyst support toward methanol oxidation. The doped CNTs were obtained by annealing PEDOT or PEDOT-based copolymer functionalized CNTs. The results indicate that the doped CNTs could significantly improve the dispersion of supported Pt nanoparticles and increase the electrochemically active surface area. The doped CNTs supported Pt-based catalysts exhibit much higher electrocatalytic activity, long-term durability and CO-tolerance ability for the methanol oxidation reaction compared to the undoped CNT supported Pt and commercial Pt/C catalysts.

Recent Publications:

1. J J Fan, Y J Fan, R X Wang, S Xiang, H G Tang, *et al.* (2017) A novel strategy for the synthesis of sulfur-doped carbon nanotubes as a highly efficient Pt catalyst support toward the methanol oxidation reaction. *J. Mater. Chem. A* 5:19467–19475.
2. R X Wang, Y J Fan, L Wang, L N Wu, S N Sun, *et al.* (2015) Pt nanocatalysts on polyindole functionalized carbon nanotubes composite with high performance for methanol electrooxidation. *J. Power Sources* 287:341–348.
3. L Wei, Y J Fan, J H Ma, L H Tao, R X Wang, *et al.* (2013) Highly dispersed Pt nanoparticles supported on manganese oxide-poly(3,4-ethylenedioxythiophene)-carbon nanotubes composite for enhanced methanol electrooxidation. *J. Power Sources* 238: 157–164.

Biography

You-Jun Fan is a Professor of Physical Chemistry at the Guangxi Key Laboratory of Low Carbon Energy Materials, College of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, China. He received his MSc Degree in 2001 from China University of Geosciences, and his PhD in 2005 from Xiamen University. He was a Post-doctoral Fellow at the Research Institute of Electronics, Shizuoka University, Japan (2005–2007). His current research interests include electrocatalysis, electrochemical energy conversion and storage, and electrochemical biosensor. He has published more than 60 research papers, in journals including *J. Mater. Chem. A*, *Nanoscale*, *J. Phys. Chem. C*, *J. Power Sources*, *Electrochem. Commun.*, *Electrochim. Acta*, *Dalton Trans.*, *Microchim. Acta*, *Mol. Catal.*, *Int. J. Hydrogen Energy*, *RSC Adv.*, etc. He has obtained 8 innovation patents, and contributed to 2 scientific books. His research interests are electrocatalysis, electrochemical energy conversion and storage, and electrochemical biosensor.

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PHOTO-DESIGN OF METAL POLYMER NANOMATERIALS AND NANOSTRUCTURES

Lavinia Balan

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The size dependent properties of noble metal nanoparticles (MNPs) have created a great promise for their use in a variety of optical, electronic and biomedical applications. Nowadays, a great diversity of techniques such as chemical, thermal, photochemical or biological and methods have been developed for their synthesis. Among them, photochemical approach has proven to be an excellent tool to synthesize nanoparticles and also nanocomposite materials in the investigation of the mechanistic aspects of their formation. In particular, we present the advantages of a “green” and “highly flexible” character and a strong control in both spatial and temporal directions. In this context, firstly, we will use photochemistry to generate MNPs through photo reduction of a metal precursor using free radicals generated from photosensitizers in an aqueous solution or directly generated onto glass surfaces in order to produce plasmonic surfaces. Thus, efficient nanoparticle synthesis and their morphological control require a careful selection of experimental conditions such as photonic and chemical parameters. Moreover, the photochemical tool was used not only for the nanoparticles synthesis, but also to obtain advanced nanomaterials as nanocomposites metal/polymer. The hybrid nanocomposites have been obtained by combing the *in situ* photoreduction of MNPs with the acrylates monomers photopolymerization. Specific interactions between the macromolecular network and the nascent particles were funded to play an important role insofar as they control the access of metal atoms to the different crystalline planes of the growing nanoparticles, which is necessary to obtain anisotropic objects. The assembling process of MNPs in the polymer matrix was the next step of our work. Controlling both the synthesis and multi-scale organization (nano, micro and macro) of such cross-linked organic-inorganic nanomaterials opens promising prospects in the field of advanced materials.

Biography

Lavinia BALAN obtained the PhD degree from the University Henry Poincaré in Nancy, France, in 2005. Her PhD was devoted to the elaboration of an original material for the anode of Li-ion batteries. After a post doctorate in Orleans and then in Mulhouse, she joined the Department of Photochemistry of Mulhouse in 2006 as a CNRS Senior Researcher. She opened a new field of research in this laboratory, viz. the photo-assisted synthesis of metal nanoparticles and metal-polymer Nano composite. Since December 2009, L. Balan joined the Institute of Materials Science of Mulhouse (IS2M)-CNRS. She has published more than 100 scientific publications, 4 book chapters and 5 patents. Dr. L. Balan has been serving as an editorial board member for few scientific journals. Lavinia BALAN research are concerned with photochemical synthesis of metal/polymer nanocomposites and design, customization and characterization of metal nanoparticles and nanocrystals (quantum dots) suited for advanced applications in the fields of optic, photonics, plasmonics, imaging or biology.

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DAY 1

March 26, 2018

Sessions

Biopolymers and Biomaterials | Polymer Physics and Characterizations

Session Chair

DESBRIERES Jacques

University of Pau and Pays Adour, France

Session Co-chair

Lavinia Balan

CNRS Institut de Science des Matériaux de Mulhouse, France

Session Introduction

Title: Advanced optoelectronic materials and devices via integrating functional polymers

Dong Ha Kim, Ewha Womans University, Republic of Korea

Title: Polymer surfaces for calcium phosphate deposition – implications for 3D printed polymer scaffolds

Andreas Taubert, University of Potsdam, Germany

Title: Bio-inspired engineering of microchannels in polymers by crystallization of solvent

Jonghwi Lee, Chung-Ang University, South Korea

Title: Core crosslinking of polymeric flower like micelles using native chemical ligation

Tina Vermonden, Utrecht University, Netherlands

Title: Electrospinning of polyheteroarylenes for new nanofiber functional materials

Ivan Ponomarev, ELMARCO s.r.o, Czech Republic

Title: Highly conducting polymers for thermoelectric applications

Jianwei XU, Institute of Materials Research and Engineering, Republic of Singapore

Title: Novel thermodynamic concepts for nucleation processes

Gerhard Eder, Johannes Kepler University, Austria

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ADVANCED OPTOELECTRONIC MATERIALS AND DEVICES VIA INTEGRATING FUNCTIONAL POLYMERS

Dong Ha Kim

Ewha Womans University, South Korea

In this presentation, we introduce our recent accomplishments on the integration of tailor-designed polymers for diverse applications. Hybrid plasmonic nanostructures comprising Au nanoparticle arrays separated from Au substrate through a temperature-sensitive poly(N-isopropylacrylamide) linker layer were constructed, and a unique plasmonic-coupling-based surface plasmon resonance sensing properties and visible light active photocatalysis were investigated. Multimetallic Core@Shell nanoparticles consisting of Au core and metal-containing polyaniline shells were prepared and their bifunctional electrocatalytic performance was systematically investigated. Well-defined ordered arrays of plasmonic nanostructures were fabricated on stretchable poly(dimethyl siloxane) substrates and tunable plasmon-coupling-based sensing properties were comprehensively demonstrated upon extension and contraction. We studied phosphorescence emission enhancement of a purely organic phosphor system via plasmon resonance energy transfer by precisely tuning the distance between purely organic phosphor crystals and plasmonic nanostructures using layer-by-layer assembled polyelectrolyte multilayers as a dielectric spacer. We demonstrate a viable laser interference lithography technique enabling the development of high-performance plasmonic organic photovoltaic (OPV) devices. Ag nanodot arrays with optimized configuration embedded in poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) hole transport layer remarkably enhanced the average power conversion efficiency by ~34.4% compared to the pristine device. Hierarchically organized porous carbonized-Co₃O₄ inverse opal nanostructures were synthesized via complementary colloid and block copolymer self-assembly, where the triblock copolymer Pluronic P123 acts as the template and the carbon source. These highly ordered porous inverse opal nanostructures with high surface area display synergistic properties of high energy density and promising bifunctional electrocatalytic activity toward both the oxygen reduction reaction and oxygen evolution reaction in Li-air battery.

Recent Publications:

1. Seol A Cho, Yu Jin Jang, Hee-Dae Lim, Ji Eun Lee, Yoon Hee Jang, *et al.* (2017) Hierarchical porous carbonized Co₃O₄ inverse opals via combined block copolymer and colloid templating as multifunctional electrocatalysts and cathodes in Li-O₂ battery. *Adv. Energy Mater* DOI: 10.1002/aenm.201700391.

2. Ji-Eun Lee, Yu Jin Jang, Wenqian Xu, Zhenxing Feng, Hee-Young Park, *et al.* (2017) PtFe catalysts supported on electroactive Au-PANI Core@Shell nanoparticles for high-performance electrocatalysis. *J. Mater. Chem. A* 5:13692–13699.
3. Yulin Oh, Ju Won Lim, Byung-Hyun Kang, Young Wook Park, Heejun Kim, *et al.* (2016) Plasmonic periodic nanodot arrays via laser interference lithography for organic photovoltaic cells with >10% efficiency. *ACS Nano* 10(11):10143–10151.
4. Ji-Eun Lee, Jumi Lee, Kyungwha Chung, Kwanwoo Shin, Dong Ha Kim, *et al.* (2015) *In situ* studies of surface plasmon resonance coupling sensor mediated by stimuli-sensitive polymer linker. *Adv. Funct. Mater.* 25(18):6716–6724.
5. Minji Yoon, Ji-Eun Lee, Ju Won Lim, Saji Thomas Kochuveedu, Yu Jin Jang, *et al.* (2015) Comprehensive study on the controlled plasmon-enhanced photocatalytic activity of hybrid Au/ZnO systems mediated by thermoresponsive polymer linkers. *ACS Appl. Mater. Interf.* 7(38):21073–21081.

Biography

Dong Ha Kim is currently a Full Professor and Ewha Fellow in the Department of Chemistry and Nano Science of School of Natural Sciences at Ewha Woman's University and Fellow of the Royal Society of Chemistry. He has authored 145 SCI publications and holds 29 registered Korean and two US patents. He is serving as Associate Editor of *Science of Advanced Materials* (American Scientific Publishers), Editorial Board Member of *Scientific Reports* (Nature Publishing Groups) and Advisory Board Member of *Nanoscale* and *J. Mater. Chem.* (Royal Society of Chemistry). His research interests include development of multi-functional hybrid nanostructures for applications in energy storage and conversion, environmental remediation, memory devices, display devices, and biomedical diagnosis/therapy, surface plasmon resonance mediated theranostics, optoelectronics, photocatalysis and light emission.

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POLYMER SURFACES FOR CALCIUM PHOSPHATE DEPOSITION – IMPLICATIONS FOR 3D PRINTED POLYMER SCAFFOLDS

Andreas Taubert

University of Potsdam, Germany

Calcium phosphate is one of the most important biominerals. Templated or biomimetic calcium phosphate mineralization provides access to a large variety of calcium phosphate composites that could for instance, be useful for bone repair. Most experiments on the formation of such composites involve the precipitation of a mineral phase from bulk aqueous solution. This process is, however, rather unrelated to true biological conditions because the effects of surfaces and interfaces are ignored. The presentation will show how model surfaces, both at the solid-liquid and the liquid-air interface, affect calcium phosphate formation. Our studies show that not only the type of surface (anionic vs. cationic) but also the charge of each polymer surface (charged vs. uncharged) and the architecture of the hydrophilic groups (dendritic vs. linear) strongly affect the outcome of the mineralization process. Finally, the presentation will demonstrate how surface chemistries such as those just discussed can be used to modify the surfaces of 3D printed polymer scaffolds and how these surface modifications affect the mineral deposition for biomaterials development.

Biography

Andreas Taubert is Professor of Supramolecular Chemistry at the University of Potsdam, Germany. After completing a Diploma at the University of Basel/Switzerland and a PhD at the Max-Planck-Institute for Polymer Research in Mainz/Germany, he was a Post-doc at the University of Pennsylvania/USA and then a Group Leader at the University of Basel. In 2006, he was appointed Junior Professor of Supramolecular Chemistry at the University of Potsdam and the Max Planck Institute of Colloids and Interfaces before accepting his current position in 2011. His research interests include hybrid materials, biomimetic materials, biomaterials, surfaces, ionic liquids, ionogels, energy materials and materials analysis.

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BIO-INSPIRED ENGINEERING OF MICROCHANNELS IN POLYMERS BY CRYSTALLIZATION OF SOLVENT

Jonghwi Lee

Chung-Ang University, South Korea

For millions of years, nature utilizes microporous polymeric materials of well-controlled structures of skeletal walls and pores for their functions. The structures of synthetic microporous polymers are commonly limited to architectures of isolated pores, although their preparation methods have been developed for the critical roles in various applications. The directional melt crystallization of solvent, a relatively new versatile preparation method to produce aligned pores in the forms of 3D patterns, has produced porous structures of Voronoi and honeycomb-like architecture morphology. By developing adequate conditions for different polymers, we have produced various materials having ordered microchannels. The important parameters, crystallization rate and direction were controlled by temperature gradient control in 3D space using a home-made apparatus to prepare defect-free materials having well-ordered through-thickness microchannels. As crystals nucleate and grow, solutes form cryoconcentrate phases, which become skeletal portions, and crystallized solvents become pores after sublimation. The defect-free films and cylinders of through-thickness porosity could be prepared. With the support of nanotemplates, nanospheres, nanorods, and nanomembranes could be prepared too. This directional crystallization method controlling pore morphology offers a versatile route to prepare unique porous polymers and composites for future environmental, biomedical, and electronics applications.

Recent Publications:

1. Junseok Kim, Yunho Cho, Soyun Kim, and Jonghwi Lee, 2017, 3D Cocontinuous Composites of Hydrophilic and Hydrophobic Soft Materials: High Modulus and Fast Actuation Time, *ACS Macro Letters*, 6(10), p1119.
2. Byoung Soo Kim, Kangsuk Lee, Soyeon Lee, Jun Beom Pyo, Kwang-Hoon Lee, In Suk Choi, Kookheon Char, Jong Hyuk Park, Sang-Soo Lee, Jonghwi Lee*, Jeong Gon Son*, 2017, 2D reentrant auxetic structures of graphene/CNT networks for omnidirectionally stretchable supercapacitors', *Nanoscale*, 9, p13272.
3. A.T. Ezhil Vilian, Suyeong An, Sang Rak Choe, Cheol Hwan Kwak, Yun Suk Huh*, Jonghwi Lee*, and Young-Kyu Han*, 2017, Fabrication of 3D honeycomb-like porous polyurethane-functionalized reduced graphene oxide for detection of dopamine, *Biosensors and Bioelectronics*, 86, p1222.
4. Byoung Soo Kim and Jonghwi Lee, 2016, Macroporous PVDF/TiO₂ membranes with three-dimensionally interconnected structures produced by directional crystallization, *Chemical Engineering Journal*, 301, p158.
5. Suyeong An, Byoung Soo Kim and Jonghwi Lee, 2016, Porous Polyurethane Films Having Biomimetic Ordered Open Pores: Indentation Properties, *Journal of Industrial and Engineering Chemistry*, 33, p362.

Biography

Jonghwi Lee got his PhD from the University of Michigan, Ann Arbor and worked for Merck Research Laboratories as a Senior Researcher after his Post-doctoral training at the University of Minnesota. He won prizes from The Polymer Society of Korea (Best Paper Award), Korean Society of Industrial Engineering Chemistry (Contribution Recognition Award, Best Paper Award, Best Industry Collaboration Award), and Chung-Ang University (Excellence in Achievement Award, Bae Young Soo Award). He has published more than 150 research papers, and currently a Vice Editor of *Journal of Industrial and Engineering Chemistry and Macromolecular Research*. His research interests are biomedical polymers, polymer composites, porous polymers and crystallization.

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Tina Vermonden, Polym Sci, Volume 4
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CORE CROSSLINKING OF POLYMERIC FLOWER LIKE MICELLES USING NATIVE CHEMICAL LIGATION

Tina Vermonden

Utrecht University, Netherlands

Native chemical ligation (NCL) is an attractive method to covalently cross-link polymers, because of its ability to react under physiological conditions avoiding the use of toxic reagents and catalysts, making this method very biofriendly. Since NCL is a very specific ligation between N-terminal cysteines and thioesters, side reactions with biomolecules can be ruled out and therefore NCL is expected to be highly compatible with encapsulated drugs. In this study, native chemical ligation (NCL) was used as a selective crosslinking method to form core-crosslinked thermosensitive polymeric micelles for drug delivery applications. To this end, two ABA triblock copolymers consisting of polyethylene glycol (PEG) as midblock and thermosensitive poly isopropylacrylamide (PNIPAM) outer blocks decorated with either cysteine (NIPAM-co-HPMA-Cys)-PEG-P(NIPAM-co-HPMA-Cys) (PNC) or thioester P(NIPAM-co-HPMA-ETSA)-PEG-P(NIPAM-co-HPMA-ETSA) (PNE) functionalities were synthesized by atom transfer radical polymerization (ATRP). Mixing of these polymers in aqueous solution followed by heating to 50°C resulted in the formation of thermosensitive flower-like micelles. Subsequently, native chemical ligation in the core of micelles resulted in stabilization of the micelles with an average diameter of 65 nm at 37°C. Decreasing the temperature to 10°C only affected the size of the micelles (increased to 90 nm) but hardly affected the polydispersity index (PDI) and aggregation number (N_{agg}), confirming covalent stabilization of the micelles by NCL. Notably, by simply adjusting the molar ratio between the polymers, the extra cysteine or thioester moieties could be used for conjugation of functional molecules. Furthermore, *in vitro* cell experiments demonstrated that fluorescently labeled micelles were successfully taken up by HeLa cells, while cell viability remained high even at high micelle concentrations. These results demonstrate the potential of these micelles for drug delivery applications.

Biography

Tina Vermonden obtained her PhD in Physical and Organic Chemistry from Wageningen University and Research Centre, and conducted her Post-doctoral training at Utrecht University. She is currently an Associate Professor in the Department of Pharmaceutics at Utrecht University and Coordinator of the Honours Program Pharmaceutical Sciences and is part of several large national and EU consortia. Her research is focussed on the development of biomaterials for tissue engineering and drug/protein delivery. Her group designs, synthesizes and characterizes polymers with special emphasis on cross-linking techniques to obtain advanced material properties for biomedical applications. Her research interests are in the fields of Biomaterials, Hydrogels, Polymeric Micelles, Drug Delivery and Regenerative Medicine.

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ELECTROSPINNING OF POLYHETEROARYLENES FOR NEW NANOFIBER FUNCTIONAL MATERIALS

Iv I Ponomarev^{1,2}, I I Ponomarev², D Yu Razorenov², K M Skupov², O M Zhigalina², Yu A Volkova², V G Zhigalina², Yu M Volfkovich² and V E Sosenkin²

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Nanostructured materials based on aromatic heterocyclic polymers, polyheteroarylenes (PHA) are now widely common in photovoltaics, membrane technologies, sensor and electrochemical devices, etc. New PHAs convertible by electrospinning to nanofiber mats are demanded on modern state of nanotechnology for example as high performance carbonaceous material of gas diffusion electrodes (GDE) for hydrogen-air polymer electrolyte membrane fuel cell (PEMFC). The spinnability of polyheteroarylenes was not a subject of large investigations. The process of PHA electrospinning is a very challenging task. There are no general methods which would allow obtaining an electrospun material certainly. Failing to find a right set of electrospinning conditions may lead to the impossibility of nanofiber formation. Hence, many parameters of the electrospinning process should be found empirically, which in some cases is a long and routine process. Only few papers describe nanofiber materials based on some polyimides, m-polybenzimidazole (m-PBI) and semi-ladder PIM-1 obtained only on so called "needle" setups. Elmarco's first "needle-free" electrospinning equipment Nanospider™ is proved by industrial operation; a technology based on spinning from a free liquid surface. Needle-free process guarantees optimal distance between Taylor cones, excellent web and fiber uniformity, simplicity of design, robustness against clogging of a spinneret, increased productivity due to the simultaneous operation of numerous jets. The lecture will be devoted to the production of new high-tech PHAs nanofibers and non-woven materials eminently suitable for electrochemical applications.

Recent Publications:

1. Skupov K M, Ponomarev I I, Razorenov D Yu, Zhigalina V G, Zhigalina O M, *et al.* (2017) Carbon nanofiber paper cathode modification for higher performance of phosphoric acid fuel cells on polybenzimidazole membrane. *Russian Journal of Electrochemistry* 53(7):728–733.
2. Zhigalina V G, Zhigalina O M, Ponomarev I I, Skupov K M, Razorenov D Yu, *et al.* (2017) Electron microscopy study of new composite materials based on electrospun carbon

nanofibers. *Cryst Eng Comm.* (RSC) 19(27):3792–3800.

3. Skupov Kirill M, Ponomarev Igor I, Razorenov Dmitry Y, Zhigalina Viktoria G, Zhigalina Olga M, *et al.* (2017) Carbon nanofiber paper electrodes based on heterocyclic polymers for high temperature polymer electrolyte membrane fuel cell. *Macromol. Symp.* 375(1):1600188–92.
4. Razorenov Dmitry Y, Skupov Kirill M, Volkova Yulia A, Ponomarev Ivan I, Chaika Elena M, *et al.* (2017) Poly(N-phenylenebenzimidazoles): a new approach for monomer synthesis. *Macromol. Symp.* 375(1):1600152–59.
5. I I Ponomarev, K M Skupov, D Yu Razorenov, V G Zhigalina, O M Zhigalina, *et al.* (2016) Electrospun nanofiber pyropolymer electrodes for fuel cells on polybenzimidazole membranes. *Russ J Electrochem* 52:735.

Biography

Ivan Ponomarev PhD. is the Head of Chemistry and Technology Department at ELMARCO s.r.o. (Czech Republic). He obtained master degree from Russian University of Chemical Technology, Moscow, Material technology and new composite material technology in the academic year 2001–2007. His master degree work was partially carried out at A N Nesmeyanov Institute of Organo-element Compounds Russian Academy of Sciences. He received PhD. Degree from A N Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Moscow in the year 2007–2010. Main topic: Synthesis of high-tech polymers for fuel cells, design of membrane electrode assemblies. From 2005–2010 he worked as Researcher at A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, where he worked on the synthesis of high-tech polymers for fuel cells, management of project part, design of membrane electrode assembly. His research interests include electrospinning, synthesis and modification of heterocyclic polymers and new nanomaterial creation. In 2010 Ivan started his career as R&D project manager at Elmarco company - world leader in industrial nanofiber equipment production based on patented Nanospider™ technology. Since 2015 Mr. Ponomarev is leading Chemistry & Technology department at Elmarco.

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Jianwei Xu, Polym Sci, Volume 4
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HIGHLY CONDUCTING POLYMERS FOR THERMOELECTRIC APPLICATIONS

Jianwei Xu

Agency for Science, Technology and Research, Singapore

Thermoelectric materials could be applied as thermal power generators to convert heat directly into electrical energy or as a solid state Peltier cooler. In general, traditional thermoelectric materials include alloy such as Bi_2Te_3 , Sb_2Te_3 , PbTe , etc. Recently, conducting polymer-based semiconductors have been gradually receiving much attention as conducting polymers are able to offer many advantages such as low cost, lightweight, flexibility and solution-process fabrication. In addition, conducting polymeric materials with intrinsically low thermal conductivity, which is over two to three orders of magnitude lower than that of commercial inorganic materials, make them as potential candidates for high performance thermoelectric applications. However, the efficiency of conducting polymeric materials is still much lower than that of inorganic counterparts such as Bi_2Te_3 and Sb_2Te_3 . The thermoelectric performance of a material is usually judged by a dimensionless thermoelectric figure of merit (ZT), which is calculated in terms of $ZT = S^2\sigma T/\kappa$, where S , σ , T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. As the thermal conductivity of conducting polymers is usually less than 1 W/mK, much work is focused on how to enhance the electrical conductivity and Seebeck coefficient or how to obtain a proper balance between electrical conductivity and Seebeck coefficient so as to achieve thermoelectric materials with a high ZT value. This presentation will highlight recent advances of highly conductive polymers including poly(3,4-ethylenedioxythiophene) and related analogous polymers for thermoelectric applications.

Biography

Jianwei Xu is currently a Principal Scientist, Strategic Research Councillor at the Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), and he is an Adjunct Research Associate Professor in the Department of Chemistry at the National University of Singapore (NUS). He is also Program Manager of the Hybrid Thermoelectric Program of Science and Engineering Research Council (SERC), A*STAR. His research interests include: functional π molecular and conjugated polymer materials for electrochromic and thermoelectric applications, organic-inorganic hybrid materials and aggregation-induced emission (AIE)-active materials.

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NOVEL THERMODYNAMIC CONCEPTS FOR NUCLEATION PROCESSES

Gerhard Eder

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Nucleation is one of the basic processes involved in phase transitions like crystallization, describing the first occurrence of entities able to grow. For a better understanding of this process, which usually starts at a nanoscopic scale, one has to introduce novel thermodynamic properties in terms of the only four basic geometrical characteristics in a two-phase system. These are the four so-called Minkowski functionals, which are: volume, interfacial area, mean curvature integral over the interfacial area and the Euler-Poincaré characteristics. The latter two quantities, although introduced already in the early 19th century, have been mainly ignored so far in natural and technical sciences. The simple assumption of linear coefficients for the work differential in terms of the differential change of the four Minkowski functionals leads (in addition to pressure and interfacial energy) to two novel energetic properties: edge force and item energy. They dominate the behaviour at structural scales in the nm range. For example, the classical Young-Laplace equation stating the proportionality of the pressure jump across an interface and the mean curvature of the interface (with twice the interfacial tension as proportionality constant) has to be extended by a second term proportional to the Gaussian curvature of the interface with the edge force as proportionality constant. As a consequence, one has in polymer melts already at temperatures above the thermodynamic melting temperature stable clusters which, however, are unable to grow. At quick cooling one finds a simple relationship for the well-known temperature of homogenous nucleation in terms of the edge force.

Recent Publications:

1. G Eder and H Janeschitz Kriegl (1997) Structure development during processing: crystallization In Materials Science and Technology. Wiley VCH. 18:269-342.
2. H Janeschitz Kriegl, G Eder, M Stadlbauer and E Ratajski (2005) A thermodynamic frame for the kinetics of polymer crystallization under processing conditions. Chem. Monthly. 136(7):1119-1137.
3. P Hierzenberger, E Leiss Holzinger, B Heise, D Stifter and G Eder (2014) *In-Situ* Optical coherence tomography for the time-resolved investigation of crystallization processes in polymers. Macromolecules. 47(6):2072-2079.
4. G Eder (2018) The role of Minkowski functionals in the thermodynamics of two-phase systems. AIP Advances. 8(1). Doi:10.1063/1.5017592.

Biography

Gerhard Eder is a Professor at the Institute of Polymer Science, Johannes Kepler University Linz, Austria. He got Diploma in Mathematics and Physics in 1982 and 1983 and finished his PhD in 1989 with a thesis on rheology of polymer melts. In 1989/90 he was Research Scientist at the Philips Natuurkundig Laboratorium in Eindhoven, Netherlands. Since 1997 he is an Associate Professor at Johannes Kepler University. In 2002, he was Visiting Professor in Yamagata University, Japan. He gave more than 20 invited lectures at international conferences. In 2013 he received the Hermann Mark Medal for his work on polymer characterization. His research interests are focused on structure development of polymers under extreme conditions as present in usual processing, a field which is situated between and strongly interacting with the classical transport phenomena: heat transfer, flow dynamics and mass diffusion. During the last few years his interest widened towards thermodynamics of phase transitions and kinetic modelling.

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DAY 2

Scientific Tracks & Abstracts



3rd Edition of International Conference and Exhibition on

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DAY 2

March 27, 2018

Sessions

Applications of Biopolymers | Recent Developments in Polymer Synthesis | Polymer Science

Session Chair
Cor Koning

DSM Coating Resins, The Netherlands

Session Chair
Mauro Giorcelli

Politecnico di Torino, Italy

Session Introduction

Title: 3D structured composite filter materials with embedded natural nano-fillers

Manja Kurecic, University of Maribor, Slovenia

Title: Renewable and sustainable coating resins

Cor Koning, DSM Coating Resins, Netherlands

Title: Giant vesicles supporting amino groups on the hydrophilic shells prepared by photo-controlled/living radical polymerization-induced self-assembly of amphiphilic block copolymers

Eri Yoshida, Toyohashi University of Technology, Japan

Title: Rapid synthesis of a novel type thermostable poly(ether)-b-poly(amide) (PEBA) with well-defined amide segments, and the application to shape memory material

Yuji Shibasaki, Iwate University, Japan

Title: All polyolefin composites via nanostructure formation during melt processing

Rolf Mülhaupt, University of Freiburg, Germany

Title: Nanocontainers based on biodegradable polymer and anionic liposomes

Anna Efimova, Moscow State University, Russian Federation

EuroSciCon

Polymer Chemistry 2018

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Manja Kurečič et al., Polym Sci, Volume 4
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3D STRUCTURED COMPOSITE FILTER MATERIALS WITH EMBEDDED NATURAL NANO-FILLERS

Manja Kurečič^{1,2}, Silvo Hribernik¹, Mojca Božič¹, Tanja Kos¹, Matej Zadravec¹
and **Karin Stana Kleinschek^{1,2}**

¹University of Maribor, Slovenia

²Graz University of Technology, Austria

Development of bio-based filtering materials follows the need for a drastic reduction in solid particle-pollution, which is nowadays one of the largest risks for human health and state of the environment. Filtering sector currently concerns itself primarily with removal and immobilization of increasingly small particles, effectively requiring small pore size and enhanced surface area. This research work is a part of a national research and development program "Cel.Cycle", aiming at constructing materials with a hierarchical porous structure and increased active surface; in order to do this, existing and novel technologies will be employed, as well as integration of active components (inorganic particles; micro- and nano-fibrillated cellulose), leading to 3D nonwoven structures with desired functional properties. The increase of organic compounds in environment encourages also search for more efficient adsorbents used in water treatment. Clays are known as natural environmental-friendly materials with high specific surface area, used in dispersed form, for the adsorption and removal of organic pollutants, causing difficult removal from purified water. Therefore, the second part of this research is focused on preparation and characterization methods

of nanocomposite clay/polymer hydrogels used for adsorption of textile dyes. Structures and functionalities of nanocomposites will be described and conditions (e.g. clay particle type and concentration, dispersing medium, monomer, cross-linker concentrations, and drying procedure, etc.) for achieving exfoliated and intercalated clay-hydrogel structures will be discussed. In addition to functional properties of nanocomposites conditioned by the nanocomposite, their preparation process will be discussed.

Biography

Manja Kurečič is a Scientific Associate at the Faculty of Mechanical Engineering, University of Maribor and Technical University Graz, Austria, where she is working on several national and international basic and applied projects. She has a background on nanocomposite hydrogels for water purification, which she upgraded with new technologies for preparation of different nanostructured materials that can find applications in technical as well as in the biomedical area. Lately, she is focusing on development of innovative nanofibrous materials by using electrospinning method.

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Cor Koning, Polym Sci, Volume 4
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RENEWABLE AND SUSTAINABLE COATING RESINS

Cor Koning

DSM Coating Resins, Netherlands

The presentation will comprise industrial and academic examples of a number of different and distinct types of sustainable coatings entirely or partly based on renewable raw materials. In one industrial example, alkyd resins were prepared from new bio-based cyclic imide building blocks which were synthesized from amino acids like lysine, glycine and phenylalanine and from di- or tricarboxylic acids like succinic acid and citric acid, respectively. These cyclic imide building blocks were incorporated into alkyd resins by standard polycondensation chemistry and technology. The resulting alkyd resins were evaluated as coating resins, either by casting films from xylene or by making coatings from water-based alkyds after emulsification of the synthesized alkyd resins. The properties of the predominantly bio-based coatings look promising, some even outperforming standard commercial alkyd resins. In an academic example, the applied raw materials were limonene mono-oxide and carbon dioxide. A Zn-catalyzed polymerization process yielded fully renewable polycarbonates. Solvent-based coatings as well as sustainable powder coatings were made from these polycarbonates and showed promising properties after curing. In another academic example, a very promising finding is demonstrated: the possibility

to polymerize limonene dioxide with carbon dioxide, yielding a nearly linear polycarbonate with one epoxide group per repeat unit. This poly(limonene oxide carbonate) was decorated with fatty acids, giving fully renewable, comb-shaped alternative alkyd resins exhibiting remarkable properties. Finally, in yet another academic example, the properties of coatings based on poly(limonene carbonate) and poly(cyclohexadiene carbonate) will be compared.

Biography

Cor Koning studied Polymer Chemistry and obtained his PhD Degree in 1987 at the University of Groningen, the Netherlands. In 1987, he joined DSM Research in Geleen, the Netherlands. In 2000, he was appointed as Full Professor at the TU Eindhoven and he left DSM. His research focus was on the synthesis and evaluation of renewable step-growth polymers and he also initiated a program on CO₂-based polycarbonates. In 2011, he joined DSM Coating Resins as Science Manager Polycondensates and was later appointed as Senior Science Fellow of Polycondensation Technology. His research interests are in the field of Polycondensates, Sustainable coatings and Epoxide-CO₂ Polymerizations.

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Eri Yoshida, Polym Sci, Volume 4
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GIANT VESICLES SUPPORTING AMINO GROUPS ON THE HYDROPHILIC SHELLS PREPARED BY PHOTO-CONTROLLED/LIVING RADICAL POLYMERIZATION-INDUCED SELF-ASSEMBLY OF AMPHIPHILIC BLOCK COPOLYMERS

Eri Yoshida

Toyohashi University of Technology, Japan

Micro-sized giant vesicles are a possible artificial model of biomembrane for cells and organelles, such as erythrocytes, mitochondria, and chloroplasts based on the similarities in size and structure. In recent years, a novel artificial biomembrane model has been established using giant vesicles comprised of amphiphilic poly(methacrylic acid)-block-poly(methyl methacrylate-random-methacrylic acid) diblock copolymers. The polymer giant vesicles had some similarities to biomembrane, not only in size and structure but also in the formation mechanisms, morphological transformation, membrane permeability, and stimulus-responsiveness. This paper describes the preparation and morphological transformation of new giant vesicles supporting amino groups on the hydrophilic shells through the nitroxide-mediated photo-controlled/living radical polymerization (photo-NMP)-induced self-assembly, with the aim of establishing an artificial model more suitable to biomembrane. The giant vesicles were prepared by the block copolymerization of a methacrylate ester supporting an amino group and methyl methacrylate using the photo-NMP technique in methanol at room temperature by irradiation with a high-pressure UV lamp. The photo-NMP-induced self-assembly produced spherical vesicles with the hydrophilic phase of the amine-containing polymethacrylate blocks and the hydrophobic core of the poly(methyl methacrylate) blocks. The size and morphology of the vesicles were dependent on the lengths of the hydrophilic and hydrophobic blocks of the copolymers. It was found that the vesicles were pH-sensitive and disrupted in an acidic solution. Their thermo-responsive behavior will be also described.

Recent Publications

1. E Yoshida (2017) Fabrication of anastomosed tubular networks developed out of fenestrated sheets through

thermo responsiveness of polymer giant vesicles. *ChemXpress* 10(1):118.

2. E Yoshida (2015) Enhanced permeability of rhodamine B into bilayers comprised of amphiphilic random block copolymers by incorporation of ionic segments in the hydrophobic chains. *Colloid Polym. Sci.*, 293: 2437.
3. E Yoshida (2015) PH response behavior of giant vesicles comprised of amphiphilic poly(methacrylic acid)-block-poly(methyl methacrylate-random-methacrylic acid). *Colloid Polym. Sci.* 293: 649.
4. E Yoshida (2014) Morphology control of giant vesicles by manipulating hydrophobic-hydrophilic balance of amphiphilic random block copolymers through polymerization-induced self-assembly. *Colloid Polym. Sci.* 292:763.
5. E Yoshida (2013) Giant vesicles prepared by nitroxide-mediated photo-controlled/living radical polymerization-induced self-assembly. *Colloid Polym. Sci.* 291:2733

Biography

Eri Yoshida is an Associate Professor at Toyohashi University of Technology. She received her Bachelor's Degree in Education from Tokyo Gakugei University and her PhD in Polymer Engineering from Tokyo Institute of Technology. After she obtained her PhD, she joined Kyoto Institute of Technology as an Assistant Professor. She also worked as a Visiting Scientist at the University of North Carolina at Chapel Hill. She has more than 100 peer reviewed scientific publications and 24 patents. She is a Member of the Editorial Board of some international journals. Her research interests include molecular self-assembly of amphiphilic copolymers, controlled/living radical polymerization, and macromolecular design using supercritical carbon dioxide.

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Yuji Shibasaki, Polym Sci, Volume 4
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RAPID SYNTHESIS OF A NOVEL TYPE THERMOSTABLE POLY(ETHER)-B-POLY(AMIDE) (PEBA) WITH WELL-DEFINED ARAMIDE SEGMENTS, AND THE APPLICATION TO SHAPE MEMORY MATERIAL

Yuji Shibasaki

Iwate University, Japan

Poly(ether-*b*-amide) multiblock copolymers (PEBA) are a class of important thermoplastic elastomers (TPE)s, due to the tuneable properties with variable polyether soft segments (SS)s that realizes the reliable mechanical strength. We have studied packing behaviour of a series of N-alkylated polyamides(1)-2) and polyimines(3), and recently developed a rapid synthetic strategy of a novel type PEBA consisting of monodisperse poly(4-*N*-methyl benzamide) (PMBA) with poly(propylene oxide) (PPO). The resulting block copolymer shows phase-segregated structure with two distinct glass transition temperatures (T_g)s of -65 and above 50°C. Considering the experimental results of no phase segregation of the copolymer based on polydisperse PMBA ($M_w/M_n > 1.4$) with PPO, the monodisperse PMBA segment should play a critical role in the phase separation behaviour. The soft segment was then replaced from amorphous PPO into crystalline poly(ethylene glycol) (PEG), resulting in considerably distinctive phase segregation behaviour, probably due to the foreclosing effect of PEG crystal phase to PMBA segment. The dual crystalline phases realize a novel shape memory polymer (SMP) as depicted in Figure 1. In our system, the temporarily shape is formed at above 60°C (melting temperature (T_m) of PEG), and fixed below the temperature. Once the material is heated above the temperature, the original shape is promptly recovered. It is noticeable that the T_m of PMBA was increased from 208 to 232°C in DSC 1st and 2nd measurements while the T_m of PEG was almost same at 52°C. The annealing of the block copolymer was performed from 200 to 240°C, affording the promotion of the higher crystalline state of PEG segment. The polarized optical microscope observation indicated the growth of the PEG crystal in this annealing treatment. The finally obtained SMP film of the block copolymer shows the tensile modulus, strength, and elongation at breaks of 233 MPa, 10 MPa, and 100%, respectively. The properties of SMP were controllable with the change of two segments within the block copolymer.

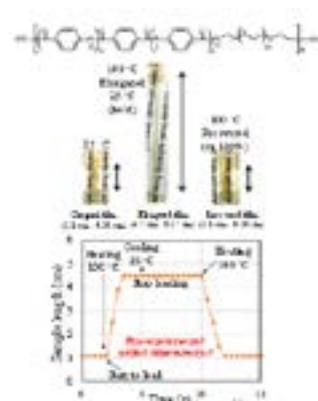


Figure 1. A novel SMP polymer based on PMBA-PEG and the SMP behavior.

Recent Publications

1. Shibasaki, Y.; Abe, Y.; Sato, N; Fujimori, A.; Oishi, Y. (2010), "Direct condensation polymerization of N-alkylated p-aminobenzoic acid and packing of rigid-rod main chains with flexible side chains.", *Polym. J.* 42, 72-80. 2) Fujimori, A.; Miura, S.; Kikkawa, Shibasaki, Y. (2014), "Fabrication and structure of "polymer nanosphere multilayered organization" *J. Polym. Sci. PART B: Polym. Phys.* 418, 338-349. 3) Miura, S., Shidara, Y., Yunoki, T., Shibasaki, Y., Fujimori, A. (2017), "High-Density Packing of Amorphous Polymer with Bulky Aromatic Rings in Interfacial Molecular Films", *Macromol. Chem. and Phys.* 218(7), 1600520. 4) Kotaki, T. Nishimura, N., Ozawa, M., Fujimori, A., Muraoka, H., Ogawa, S., Korenaga, T., Suzuki, E., Oishi, Y., Shibasaki, Y. (2016), "Synthesis of highly refractive and highly fluorescent rigid cyanuryl polyimines with polycyclic aromatic hydrocarbon pendants", *Polymer Chemistry* 7, 1297-1308. 5) Mori, T., Masukawa, S., Kikkawa, T., Fujimori, A., Satoh, A., Matsumoto, K., Jikei, M., Oishi, Y., Shibasaki, Y. (2017), "Rapid synthesis and properties of segmented block copolymers based on monodisperse aromatic poly(N-methyl benzamide) and poly(propylene oxide)" *RSC Advances* 7, 33812-33821.

Biography

Yuji Shibasaki is an Associate Professor in Polymer Chemistry at Iwate University, Japan. He studied Material Chemistry in Tokyo Institute of Technology (TIT) under the guidance of Professor Y Imai, and Polymer Chemistry at TIT under Professor T Endo. He received his PhD in 2000 for research of controlled ring-opening polymerization of lactones and cyclic carbonates. He worked as an Assistant Professor until 2007 in TIT. He engaged in Nanoparticle Chemistry in a Taton Research Group in the University of Minnesota (USA) from 2005 to 2006. His current research interests are in the synthesis of well-defined polymers, synthesis of bioinspired materials, and development of functional polymeric materials.

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Rolf Mülhaupt Alexander Kurek et al., Polym Sci, Volume 4
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ALL POLYOLEFIN COMPOSITES VIA NANOSTRUCTURE FORMATION DURING MELT PROCESSING

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Among polymeric materials, polyolefins are clear leaders with respect to both world production scale and sustainability. Produced in solvent-free and environmentally friendly processes, they combine high resource-, eco-, energy- and cost-efficiency with low weight and outstanding versatility in terms of properties, processing, applications, and recycling. However, to compete with metals they require reinforcement by alien materials which impair recycling and processing. Special processing technologies such as lamination of stretched tapes and fiber technology are required to produce "all polyolefin composites" in which both matrix and reinforcing phases consist of polyolefin. At the beginning of the 21st century, remarkable progress in multisite polymerization catalysis enables to produce reactor blends with tailored molar mass distribution which form extended-chain polyolefin during injection molding and extrusion, typical for commodity polyolefins. Robust chromium sites produce nanophase-separated ultrahigh molar mass polyethylene (UHMWPE) unaffected by other sites during ethylene polymerization on supported multisite catalysts. The site blend ratio governs ultrabroad PE molar mass distributions and nanostructures with unprecedented precision. Owing to significantly reduced UHMWPE entanglement, reactor blends with high UHMWPE content (>20 wt.-%) are melt processable by classical injection molding. HDPE wax serves as a processing aid which cocrystallizes and does not cause emission and odor problems. This *in situ* formation of nanophase-separated fiber-like extended chain UHMWPE, with an average diameter of 80 nm, effectively reinforces the HDPE matrix as expressed by significantly improved strength/stiffness/toughness balance. In addition to tailoring two- and three-site catalysts systems and reactor blends, nanophase-separated UHMWPE embedded in HDPE wax represents a versatile new additive enabling fabrication of all-polyethylene composites by melt compounding without affecting ethylene polymerization of commodity polyethylenes. Hence, this versatile route to sustainable all-polyethylene composites holds great promise for converting commodity polyolefin materials into high performance engineering materials without impairing melt processing, sustainability and facile recycling. Unlike common polyolefin nanocomposites, neither handling of problematic nanofillers nor special composite processing is required.

Recent Publications

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2. F. Zhong; J. Schwabe; D. Hofmann; J. Meier; R. Thomann, M. Enders, R. Mülhaupt (2018) All-polyethylene composites reinforced via extended-chain UHMWPE nanostructure formation during melt processing, *Polymer* 140, 107.
3. M. Stürzel; T. Hees; M. Enders; Y. Thomann; H. Blattmann; R. Mülhaupt (2016), Nanostructured Polyethylene Reactor Blends with Tailored Trimodal Molar Mass Distributions as Melt-Processable All-Polymer Composites, *Macromolecules* 49, 8048.
4. M. Stuerzel; A. Kurek; T. Hees; Y. Thomann; H. Blattmann; R. Mülhaupt (2016) Multisite catalyst mediated polymer nanostructure formation and self-reinforced polyethylene reactor blends with improved toughness/stiffness balance, *Polymer* 102, 112.

Biography

Prof. Dr. Rolf Mülhaupt studied chemistry at University of Freiburg, Germany (1973-1978) and got his PhD (1981) at ETH Zürich, Switzerland. After industrial research at DuPont Central Research (1981-1985) in Wilmington, DE, USA, and at Ciba-Geigy AG (1985-1989) in Marly, Switzerland, since 1989 he is full professor for macromolecular chemistry and director of the Institute of Macromolecular Chemistry at the University of Freiburg, Germany. Since 1992 he is the managing director of the Freiburg Materials Research Center, FMF, at the University of Freiburg, Germany. His research focuses on polymer chemistry and engineering, sustainable materials, polymerization catalysis & polyolefins, functional polymer and tailoring polymer systems, reactive processing and 3D-printing. He has published 456 papers in refereed journals and is listed as coinventor of 106 patent applications. He was awarded the Silver Medal of ETH-Zürich (1981), Piero Pino Gold Medal of the Italian Chemical Society (2004), Hermann Staudinger Price of the German Chemical Society (2009) and the Hermann F. Mark Medal (2013).

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NANOCONTAINERS BASED ON BIODEGRADABLE POLYMER AND ANIONIC LIPOSOMES

Efimova A A, Mulashkin F D, Krivtsov G G, Melik-Nubarov N S, Grozdova I D, Rudenskaya G N, Sybachin A V, Chvalun S N, Kulebyakina A I, Razuvaeva E V and Yaroslavov A A

Lomonosov Moscow State University, Russia

Liposomes are widely used in medicine for encapsulation of biologically active compounds. Multi-liposome assembly composed of liposomes loaded with different fillings could enable controlled delivery of the medicines in a desirable ratio. In this work, we suggest a universal approach for preparation of biodegradable multiliposomal containers through electrostatic adsorption of liposomes on the surface of polymer nanoparticles. Firstly, we describe the preparation and properties of nanoconjugates with the "core-shell" structure in which the micellar core from a block copolymer of polylactide and polyoxyethylene is covered by a monolayer of small unilamellar liposomes. It was shown that one micelle could bind 5–6 anionic liposomes. The resulting nanoconjugate was stable in a physiological solution with [NaCl] = 0.15 M. At the same time, the nanoconjugate degraded, being attacked by proteolytic enzymes, down to 10–15 nm particles, that was accompanied by a complete release of the encapsulated antitumor antibiotic doxorubicin into surrounding solution. In the second part of the study, anionic liposomes were adsorbed on the surface of cationic chitosan nanoparticles. Chitosan is a commercially available polycationic biopolymer of natural origin that is known for being biocompatible and biodegradable. Each chitosan particle could adsorb up to 100 anionic liposomes. The conjugates demonstrated stability towards dissociation in physiological media. The complexes were biodegradable, which eventually decomposed after addition of enzymes. It was found that chitosan-liposome complex and the products of its biodegradation were non-toxic in a wide range of concentrations. Thus, the findings of this work seem to be promising in the field of drug delivery. This work was supported by the Russian Science Foundation (project no. 14-13-00255).

Recent Publications

1. Yaroslavov A A, Efimova A A, Rudenskaya G N, Melik-Nubarov N S, Grozdova I D, et al. (2017) An electrostatic conjugate composed of liposomes, polylysine and a

polylactide micelle: a biodegradability–cytotoxicity relationship. *Mendeleev Communications* 27(3):299.

2. Sybachin A V, Zaborova O V, Efimova A A, Ballauff M and Yaroslavov A A (2017) Electrostatic complexes of liquid and solid liposomes with spherical polycationic brushes. *Polymer Science-Series C* 59(1):60.
3. Efimova A A, Chvalun S N, Kulebyakina A I, Kozlova E V and Yaroslavov A A (2016) Synthesis and properties of conjugates involving liposomes, a linear polymer, and the micelle of a polylactide–poly(ethylene glycol) block copolymer. *Polymer Science-Series A* 58(2):172.
4. Efimova A A, Zaborova O V and Sybachin A V (2016) Multiliposomal nanocontainers based on anionic solid liposomes and spherical polycationic brushes. *Materials Science and Engineering* 1(111):22.
5. Efimova A A, Sybachin A V, Chvalun S N, Kulebyakina A I, Kozlova E V, et al. (2015) Biodegradable multiliposomal containers. *Polymer Science-Series B* 57(2):140.

Biography

Anna A. Efimova graduated from Faculty of Chemistry, M.V. Lomonosov Moscow State University. In 1996 defended Ph.D. thesis. Since 1996- Research Scientist, since 2008- Associate Professor at Polymer Department of Moscow State University. In 2004 awarded with the certificate of honour of the Ministry of Education. Author or co-author of more than 40 scientific publications. Research interests are associated with the interaction of polymers and interpolymer complexes with colloid and liposomal dispersions, structural rearrangements in lipid bilayers under the polymer adsorption, polymer-induced transport of small molecules through the lipid membrane, adsorption of liposomes on the surface of (bio) colloids, biodegradable and stimuli-sensitive multiliposomal containers for the immobilization of biologically active substances..

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DAY 2

March 27, 2018

Sessions

**Polymer Engineering | Future Market of Polymers
| Polymer Design and Reactions**

Session Chair

Anna Efimova
Moscow State University, Russian
Federation

Session Co-chair

Céline Croutxé-Barghorn
Laboratory of Photochemistry and
Macromolecular Engineering, France

Session Introduction

Title: Boronic ester and homodimerization of molecular clips as cross-link motifs in the reversible networks

Monika Gosecka, Polish Academy of Sciences, Poland

Title: Estimation method of lifetime by the hydrolysis of polymer material

Yuko Sawada, Mitsubishi Electric Corporation, JAPAN

Title: High mechanical strength of supramolecular gels formed via hydrazone reaction

Jong Hwa Jung, Gyeongsang National University, South Korea

Title: Photopolymerisation of siloxane-thiol-acrylate oligomers

Vladimir Shelkovnikova, Siberian Branch of the Russian Academy of Sciences, Russia

Title: Effective anionic UV curing for a thermally dismantlable photoadhesive having disulfide bonds

Masahiro Furutani, Tokyo University of Science, Japan

Title: Polyvalent tools for polymerization under irradiation

Céline Croutxé-Barghorn, Laboratory of Photochemistry and Macromolecular Engineering, France

Title: Structuring of cellulose (nano) substrates into functional porous materials

Silvo Hribernik, University of Maribor, Slovenia

Title: Biochar as a high performance low cost filler for polymer composites

Mauro Giorcelli, Politecnico di Torino, Italy

EuroSciCon

Polymer Chemistry 2018

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Monika Gosecka, Polym Sci, Volume 4
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BORONIC ESTER AND HOMODIMERIZATION OF MOLECULAR CLIPS AS CROSS-LINK MOTIFS IN THE REVERSIBLE NETWORKS

Monika Gosecka

Polish Academy of Sciences, Poland

Polyglycidol of hyperbranched architecture (HbPGL) is able to interact with boronic acids thanks to vicinal diol groups present in the peripheral area of the macromolecule. As a result, injectable hydrogel systems can be formed at different pH conditions. Bioinert and protein antifouling characteristics of HbPGL makes hydrogels prepared from this polymer a suitable system for biomedical applications. Hydrogel environment turned out to be completely inert to alkaline phosphatase, which facilitated triggering the biomineralization

Due to the fact that diffusion of reagents limits the rate of enzymatic reactions within gel, the influence of polymer weight fraction and the length of cross-linking copolymer bearing boronic acid on the diffusivity of encapsulated in hydrogel molecules was estimated. The dynamics of macromolecules forming hydrogel network was monitored based on their diffusion coefficients using ¹H HR MAS DOSY NMR. Depending on the diffusivity, the course of biomineralization within hydrogel was different. ¹H NMR DOSY NMR spectra, along with standard ¹H NMR spectra, were also used to monitor the behaviour in solution of another type cross-link, which is a homodimer of molecular clips. By making use of this affinity, we can prolong the macromolecule

of the polymer or generate the polymer network. The affinity toward homodimerization is strictly dependent on the solvent, temperature and on the presence of other compounds, which can play the role of the guest molecules. Due to the fact that homodimerization is driven both by π - π interactions and hydrogen bonds formation, such solvents as DMSO prevents dimers formation, whereas for example chloroform stimulates the self-association of molecular clips.

Biography

Dr. Monika Gosecka is an adjunct in the Department of Engineering of Polymer Materials in the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, CMMS PAS, Lodz. She obtained her PhD degree in 2013 at the CMMS PAS for investigating the mechanism of core-shell polymer particles formation and their properties. After PhD studies, she spent a one-year as a postdoc at École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris working on the project involving vitrimer systems. Her current research interests include the formation of reversibly cross-linked hydrogels based on hyperbranched polyglycidol in view of biomedical applications.

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ESTIMATION METHOD OF LIFETIME BY THE HYDROLYSIS OF POLYMER MATERIAL

Yuko Sawada and **Daisuke Echizenya**

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Large quantities of polymer materials are used in electrical products. However, strength of the polymer material decreases under environmental condition, such as temperature, humidity and so on. Polybutylene terephthalate and polycarbonate are commonly used in the electrical products but hydrolyzed easily. Therefore, it is necessary to estimate the lifetime of polymer materials under customer environment. The long duration of conventional accelerated temperature and humidity stress test is a serious problem that exists. For the accelerated temperature and humidity stress test, we made a variety of conditions of temperature and humidity by use of constant temperature and humidity apparatus using unsaturated superheated steam. We measured the strength of polymer materials by bending test. The time at which the strength decreased by hydrolysis was related

with water vapor pressure and calculated; this was done with the estimated time under different temperature and-humidity conditions, using Arrhenius equation. To estimate the time under customer environment becomes possible and evaluation time could be reduced.

Biography

Yuko Sawada received the B.E. degree in applied chemistry from Osaka Prefecture University in 1985, and in mechanical engineering of Osaka University, Osaka, Japan. She was engaged in the research of the polymer materials at the Advanced Technology R&D Center, Mitsubishi Electric Corporation, Hyogo, Japan.

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HIGH MECHANICAL STRENGTH OF SUPRAMOLECULAR GELS FORMED VIA HYDRAZONE REACTION

Jong Hwa Jung

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Supramolecular gels comprised of low-molecular-weight gelators are generally regarded as mechanically weak and unable to support formation of free-standing structures, hence, their practical use with applied loads has been limited. Here, we reveal a technique for *in situ* generation of high tensile strength supramolecular hydrogels derived from low-molecular-weight gelators. By controlling the concentration of hydrochloric acid during hydrazone formation between calix[4]arene-based gelator precursors, we tune the mechanical and ductile properties of the resulting gel. Organogels formed without hydrochloric acid exhibit impressive tensile strengths, higher than 40 MPa, which is the strongest among self-assembled gels. Hydrogels, prepared by solvent exchange of organogels in water, show 7,000-10,000-fold enhanced mechanical properties because of further hydrazone formation. This method of molding also allows the gels to retain shape after processing, and furthermore, we find organogels

when prepared as gel electrolytes for lithium battery applications to have good ionic conductivity.

Biography

Jong Hwa Jung received his PhD Degrees in Chemistry from Gyeongsang National University and Kyushu University, Japan in 1993 and 2005, respectively. From 1994 to 2005, he worked as a Postdoctoral Fellow at Osaka University, as a Research Scientist at the Japan Science and Technology Corporation, and as a Principal Researcher at the Korea Basic Science Institute respectively. He has been a Professor in the Department of Chemistry at Gyeongsang National University since 2006. His research interest involves: supramolecular chemistry, organic-inorganic hybrid nanomaterials, functional silica-based nanomaterials, sol-gel chemistry, self-assembled gels, molecular recognition based nanosensors.

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PHOTOPOLYMERIZATION OF SILOXANE-THIOL-ACRYLATE OLIGOMERS

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Photosensitive polymer materials are prospective for the development of optical elements in integrated and diffractive optics. For this purpose, photopolymer hybrid organic-inorganic compositions are actively developed and studied. Acrylate groups, which can undergo free-radical photopolymerization, are frequently used as monomer groups in such materials. When multifunctional acrylates are used, a cross-linked polymer is formed by the action of UV light. It is accepted that the disadvantage of free-radical photopolymerization in thin films is its inhibition by atmospheric oxygen. This inhibition results from the formation of peroxide radicals, which traps free radicals and prevent further polymerization. It is known that the use of thiol compounds in acrylate photopolymer compositions helps to eliminate the oxygen inhibition of radical polymerization. The synthesis of hybrid oligomers for photopolymer compositions was carried out based on the thiolene reaction between the tetraacrylate dihydroxydiphenylsulfide derivative and siloxane-thiol oligomer. Siloxane-thiol oligomer was synthesized by condensation of diphenylsilanediol and 3-(mercaptopropyl)-trimethoxysilane. The siloxane-thiol oligomer structure was identified by ¹H, ¹³C, ²⁹Si NMR spectroscopy including COSY, HSQC, and HMBC methods and by MALDI-TOF mass spectrometry. The hybrid oligomers were obtained at different tetraacrylate: siloxane-thiol oligomer ratios. The obtained compositions were resistant to the oxygen inhibition of photopolymerization and give flexible, thermostable, and rigid polymer films under UV light. The degree of the film photopolymerization was monitored by IR spectroscopy. The thermomechanical properties of photopolymer films were determined using thermogravimetric, differential scanning calorimetric, and dynamic mechanical analyses. The storage modulus (E_0) at room temperature (1.16–1.88 GPa) and the glass transition temperatures (78–133°C) were determined for photopolymer films obtained at different ratios of acrylate and thiolsiloxane units. The photocured hybrid films exhibit high stability to thermal decomposition in the inert (T10% over 321 °C) and oxidizing (T10% over 314°C) atmospheres. The kinetics of thiol-enol photopolymerization of a hybrid composition based on a tetraacrylate monomer and a thiol-siloxane oligomer was studied with the use of a holographic recording of elementary transmission phase gratings. The degrees of conversion of double bonds in the tetraacrylate monomer after the polymerization in air and in an inert atmosphere of SF₆ were measured via IR spectroscopy. It is shown that the use of the thiol-siloxane oligomer efficiently suppresses oxygen inhibition of the photopolymerization. An increase in the thiol-siloxane oligomer concentration leads to an extremal dependence of the photopolymerization rate on the oligomer concentration; the maximum rate is reached at an oligomer concentration of about 0.07 mol/L. The kinetic scheme of photopolymerization in the hybrid photopolymer composition was analyzed, and an analytical expression for the photopolymerization

rate was obtained. The correlation between the kinetic constants of the thiol-enol photopolymerization was evaluated on the basis of the obtained parameters of the kinetic model. The results of the laser recorded structures in the hybrid polymers are represented.

Acknowledgement. The authors are grateful to the RSF (grant N 16-13-10156) for the financial support.

Recent Publications

1. I Yu Kargapolova, NA Orlova, KD Erin and V V Shelkovnikov (2016) Synthesis of unsymmetrical thioflavylium dyes from julolidine derivatives and polyfluorinated triphenyldihydropyrazoles. *Russian Journal of Organic Chemistry* 52(1)37–41.
2. V V Shelkovnikov, D I Derevyanko, L V Ektova, N A Orlova, V A Loskutov, et al. (2016) Photopolymerization kinetics of a thiol-enol composition determined via recording/playback of a transmission holographic diffraction grating. *Polymer Science Series B* 58(5)519–528.
3. N G Mironnikov, V P Korolkov, D I Derevyanko, V V Shelkovnikov, O B Vitrick, et al. (2016) Study of optical and thermo-optical properties of a hybrid photopolymer material based on thiol-siloxane and tetraacrylate oligomer. *Optoelectronics, Instrumentation and Data Processing* 52(2):180–186.
4. V V Shelkovnikov, G A Lyubas and S V Korotaev (2016) Enhanced reflective interference spectra of nanoporous anodic alumina films by double electrochemical deposition of chemical metal nanoparticles. *Nanoscale and Nanostructured Materials and Coatings, Protection of Metals and Physical Chemistry of Surfaces* 52(2)227–231.
5. E F Pen, I A Zarubin, V V Shelkovnikov and E V Vasil'ev (2016) Method for determining the shrinkage parameters of holographic photopolymer materials. *Optoelectronics, Instrumentation and Data Processing* 52(1)60–69

Biography

Vladimir Shelkovnikov is Head of Laboratory of the Light-Sensitive Materials in the Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences. Education: Tomsk Polytechnical Institute, Tomsk, USSR, 1978, Chemistry, Radiation Chemistry, Chemical Technology Engineer; Kemerovo State University, Kemerovo, USSR, 1984; PhD in Physical Chemistry; Institute of Inorganic Chemistry, Novosibirsk, Russia, 2009, Degree Doctor of Science in Physical Chemistry. His field of research interests are chemistry and photonics of the organic chromophores and polymer compositions. He has more than 30 years of varied experience in chemistry and photonics of organic medium.

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EFFECTIVE ANIONIC UV CURING FOR A THERMALLY DISMANTLABLE PHOTOADHESIVE HAVING DISULFIDE BONDS

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Photo-triggered adhesion is one of important technologies in efficient manufacture of products such as home appliances and electronic components. These products will be dismantled into their parts after use, for reusing and recycling. Today, adhesive materials are required to satisfy both strong adhesive strength and dismantling ability. In my presentation, a thermally dismantlable photo-adhesive system has been proposed. This system utilizes two key reactions, i.e. *base proliferation reaction* and *disulfide-disulfide exchange reaction*. The former is for effective anionic UV curing, or photo-adhesion, and the latter is for thermally dismantlement of adhered parts. *Base proliferation reaction*, proposed by Prof. K. Arimitsu (*K Arimitsu, M Miyamoto, K Ichimura (2000) Applications of a nonlinear organic reaction of carbamates to proliferate aliphatic amines Angew. Chem. Int. Ed. 39(19): 3425-3428.*), is a base-catalysed autocatalytic reaction of chemical compounds named base amplifiers (BAs), to enhance photo-sensitivities of materials for photo-patterning and anionic UV curing with photobase generators (PBGs). Using BA with PBG, photo-triggered *base proliferation reactions* are progressed to generate more basic species than from only PBG, under the same UV irradiation condition. Photo-adhesion is effectively realized by using BAs, because the adhesive strength is based on formation of rigid cross-linked networks resulting from reactions of resins with bases from BAs. In our case, both hard films and adhesion samples were successfully fabricated with a PBG, a bi-functional BA, and a bi-functional epoxy resin, after UV irradiation at a wavelength of 365 nm (5000, 10000, or 20000 mJ cm⁻²) and subsequent postbaking at 160°C for 10 or 30 min. In the adhesion process, photo-triggered *base proliferation reactions* between

PBGs and BAs are caused, followed by addition reactions between generated diamines and epoxy resins. On the other hand, *disulfide-disulfide exchange reaction* is one of equilibrium reactions. This reaction proceeds between two disulfide bonds via radical or ionic process under relative mild conditions, even at room temperature. Disulfide bonds have been integrated into self-healing materials of lower glass transition temperature (T_g). In our case, both a diamine from BA and a bi-functional epoxy resin have a disulfide bond in their chemical structures. The cross-linked networks fabricated with them also have many disulfide bonds, and it was found that the value of T_g was 63°C. Therefore, the adhesive strength is kept at room temperature. However, the strength became weak at 100°C (above T_g), due to the *disulfide-disulfide exchange reactions* as well as thermal relaxation of the cross-linked networks. When a shear force is added to the cross-linked networks with gentle heating, a microscopic stress is added to the disulfide bonds located in the part having high internal stress. Then, these bonds would take their interchange reactions for releasing the stress. This stress relaxation results in separating two cured bulks.

Biography

Masahiro Furutani has completed his PhD in Engineering from The University of Tokyo in 2013. He is now a research associate of Pure and applied chemistry in Tokyo University of Science, working under Professor Koji Arimitsu in the area of UV curing systems of kinds of resins for the applications of coatings and adhesives.

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PHOTOBASE GENERATORS: POLYVALENT TOOLS FOR POLYMERIZATION UNDER IRRADIATION

Céline Croutxé-Barghorn, David Perrot, Ahmad Ibrahim and Xavier Allonas

Laboratory of Photochemistry and Macromolecular Engineering, France

Photochemical generation of free radicals and acids is a widely used process in photopolymerization reactions. Recently, photobase generators (PBG) systems have emerged as new source of initiating species allowing the catalysis of different reactions (thiol-Michael, thiol-isocyanate, thiol-epoxy...). The versatility of PBGs will be highlighted through different examples. The process of light-triggered polymerization of dopamine will be first described. Irradiation of quaternary ammonium salts of phenylglyoxylic acid used as photobase generators activates the release of a strong base in water followed by an important pH jump. This initiates the polymerization of dopamine, leading to an on-demand formation of highly adhesive coating on steel. Then, photopolymerization of a thiol/epoxy/isocyanate ternary network was thoroughly investigated. Polymerization kinetics demonstrated that the thiol-isocyanate reaction is completed in a matter of seconds while the thiol-epoxy reaction exhibits a catalytic character over a few days leading to a post-consolidation of the coating. Moreover, the presence of the thiourethane network enhances the thiol-epoxy properties by increasing the

physical cross-linking due to higher content of hydrogen bonding. Compositional variations between thiol/epoxy and thiol/isocyanate and the resulting final thermomechanical properties and hardness offer many advantages in the development of materials with tunable properties.

Biography

Céline Croutxé - Barghorn graduated in chemistry at the University of Bordeaux (France) and the Technische Hochschule of Darmstadt (Germany). She attained her PhD in physical chemistry in 1996 at the University of Haute Alsace (France). Her work focused on the use of photopolymers for the generation of optical elements. She is currently Professor at University of Haute Alsace and head of the research group "Photochemistry in Organic and Hybrid Materials" (POHM) in the Department of Photochemistry. Her present research interest is the study of the photopolymerization processes in hybrid sol-gel glasses, nanocomposites and all organic resins and their characterization for specific applications (coatings or bulk materials).

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STRUCTURING OF CELLULOSE (NANO) SUBSTRATES INTO FUNCTIONAL POROUS MATERIALS

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¹University of Maribor, Slovenia

²Graz University of Technology, Austria

Cellulose fibres offer themselves as an efficient platform for development of bio-based porous matrices, which can target numerous applications. Either exploiting their supramolecular arrangement of organized fibrillar stacks within the fibre bulk for the preparation of a porous platform or breaking down its hierarchical and multi-level organization to prepare different kinds of nanoscaled cellulosic substrates, cellulose substrates offer a myriad of possibilities. In the presented study, the following two approaches will be tackled: (i) activation procedures for enhancement of cellulose fibres' accessibility and reactivity through opening and widening of voids on the surface and internal pores, by disrupting fibrillar aggregates and thus forming additional available surface and (ii) employing different nanocellulosic building blocks to create new materials through templating, with special attention given to fabrication of aerogels with controlled porosity. Mechanisms of cellulose fibre swelling and its subsequent influence on the activation of pore system will be elaborated upon and strategies for structuring of nanocellulosic

substrates, towards obtaining functional porous matrices, will be presented. Morphological, structural and chemical properties of modified fibres and newly formed structures were extensively characterized.

Biography

Silvo Hribernik works as a Scientific Associate at the Faculty of Mechanical Engineering, University of Maribor. He finished his Graduation in 2005 in the field of Eco-Textile Engineering and Doctorate in 2010 in the field of Textile Technology, from the Faculty of Mechanical Engineering in Maribor, Slovenia. During this time, he also performed research work as a Visiting Scientist at Institute of Chemistry in Ljubljana and at the Fraunhofer Institute in Potsdam, Germany. Main area of his research is the development of fibre-based functional materials with implementation of nanotechnology and is comprised of several research interests including study of materials' structure, synthesis of nano-particles, with special attention to magnetic and conductive particles, study and development of coating and adsorption processes.

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BIOCHAR AS A HIGH PERFORMANCE LOW COST FILLER FOR POLYMER COMPOSITES

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Polymer composite is a hot topic for a huge number of applications. From aerospace to everyday life, composites are becoming very popular. However, two issues have to be duly considered when a large-scale application is targeted, namely the economic and the environmental impact point of view. For the first, it will be critical to decrease the composite price while improving the properties (e.g. mechanical, electrical ones). For the second, to use of recycled or bio-derived materials is sought. In particular, in the field of polymer composites with carbon fillers, a recent trend is to use biochar in substitution to the other carbon fillers (e.g. carbon nanotubes, graphene). Biochar is a charcoal used normally as a soil amendment in agriculture. However, as it is stable and rich in carbon. Because of its high carbon content, it is a good candidate as a substitute for costlier and higher environment impact carbon forms. In this work, we will present recent achievements in the field of polymer composite based on biochar and will compare results obtained used biochar with those obtained with the other carbon fillers.

Recent Publications

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Biography

Mauro Giorcelli is a Researcher in the Department of Applied Science and Technologies, Polytechnic University of Turin, Italy. He is a Carbon Material Specialist, particularly in composites materials. He is currently working in the field of low cost carbon materials, in particular carbon materials derived from biomass (Biochar). His research interest includes: carbon materials, composite, biomaterials. He has a widespread collaboration network in Europe and Canada for biochar applications. He has published over 50 articles in international journals and they have over 500 citations.

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DAY 3

Scientific Tracks & Abstracts



3rd Edition of International Conference and Exhibition on

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DAY 3

March 28, 2018

Sessions

Bioplastics | Polymers for Emerging Technology
Polymerization Catalysis or Polymer-Modified
Catalysts | Future Market of Polymers | Applications
of Biopolymers

Session Chair
Daniel E Weibel

Federal University of Rio Grande do Sul, Brazil

Session Co-chair
Yi Liu

Lawrence Berkeley National Laboratory, USA

Session Introduction

Title: UV-surface treatment of fungal resistant polyether polyurethane film-induced growth of entomopathogenic fungi

Daniel E Weibel, Federal University of Rio Grande do Sul, Brazil

Title: 3D printing of biocomposite of polylactic acid and lignin modified cellulose nanofibrils

Mojca Bozic, University of Maribor, Slovenia

Title: Tuning structure and ordering in semiconducting conjugated polymers

Yi Liu, Lawrence Berkeley National Laboratory, USA

Title: New digital memory devices fabricated with DNA and DNA-mimics

Moonhor Ree, Pohang University of Science and Technology, South Korea

Title: Novel polymer latexes by photoactivated ring-opening metathesis polymerization in miniemulsion via the *in situ* generation of ruthenium-arene catalyst through photolabile N-heterocyclic carbene ligand

Loïc PICHAVANT, Laboratoire de Chimie des Polymères Organiques, France

Title: Silver metallization and selective metallization by spraying on 3D printed parts

Koen Staelens (Talk will be delivered by **Samuel Stremdoerfer**), Jet Metal Technologies, France

Title: Efficient optical and mechanical responses of a hydrophobic association hydrogel

Silas Owusu-Nkwantabisah, Eastman Kodak Company, USA

Title: Polymer nano-structuring induced one-shot fabrication of monodisperse gold nanoparticles relevant for SERS

Akil Suzanna, Université de Lorraine, France

EuroSciCon

Polymer Chemistry 2018

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Daniel Eduardo Weibel, Polym Sci, Volume 4
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UV-SURFACE TREATMENT OF FUNGAL RESISTANT POLYETHER POLYURETHANE AND POLYSULFONE FILMS-INDUCED GROWTH OF ENTOMOPATHOGENIC FUNGI

Daniel Eduardo Weibel

Federal University of Rio Grande do Sul, Brazil

Synthetic polymers are the cause of some major environmental impacts due to their low degradation rates. Polyurethanes (PU) and polysulfone (PSU) are widely used synthetic polymers, and their growing use in industries has caused an increase in plastic waste. A commercial polyether-based thermoplastic PU with hydrolytic stability and fungus resistance was only attacked by an entomopathogenic fungus, *Metarhizium anisopliae*, when the films were pre-treated with ultraviolet (UV) irradiation in the presence of reactive atmospheres. The same results were obtained for PSU films. The films were mainly characterized by WCA, FTIR-ATR, SEM, and optical profilometer measurements. Permanent hydrophilic PU and PSU films were produced by the UV-assisted treatments. Pristine polyether PU and PSU films incubated for 10, 30, and 60 days did not show any indication of fungal growth. On the contrary, when using oxygen in the UV pre-treatment, a layer of fungi spores covered the sample, indicating a great adherence of the microorganisms to the polymer. However, when acrylic acid vapors were used during the UV pre-treatment, a visible attack by the entomopathogenic fungi was observed. SEM and FTIR-ATR data showed clear evidence of fungal development; growth and ramifications of hyphae on the polymer surfaces with the increase in UV pre-treatment time and fungus incubation time. The results indicated that the simple UV surface activation process has proven to be a promising alternative for polyether PU and PSU waste management.

Biography

Daniel Eduardo Weibel studied Chemistry (Diploma) at the National University of Córdoba (UNC), Argentina and obtained his PhD in Physical Chemistry from University of North Carolina. He spent his Post-doctoral period at the University of Gakushuin (Japan), Munster University, (Germany) and Manchester University, (UK). He is currently an Associate Professor at the UFGRS, Brazil. He has experience in the field of Physical-Chemistry and in particular in surface science acting on the following topics: synchrotron radiation, polymers and photochemistry. His research has wide applications in self-cleaning and protective coatings, biomaterials, biocompatibility and biodegradation, photocatalysis and hydrogen generation by the water splitting reaction. His research interests also include surface science and surface modification of polymers.

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Mojca Božič et al., Polym Sci, Volume 4
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3D PRINTING OF BIOCOMPOSITE OF POLYLACTIC ACID AND LIGNIN MODIFIED CELLULOSE NANOFIBRILS

Mojca Božič¹, Silvo Hribernik¹, Manja Kurečič^{1,2}, Barbara Kaker¹, Janez Slapnik³, Silvester Bolka³ and Karin Stana Kleinschek^{1,2}

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The incorporation of lignocellulosic materials as a reinforcing component in polymer composites has received increased attention, primarily as industry attempts to lessen the dependence on the unrenowned petroleum supplies and to follow the concept of a circular economy. Nanofibrillated cellulose (NFC), derived from cellulose, the most abundant biopolymer, is one of the most promising materials. One of the key issues that have been largely investigated is the compatibility of the NFC with polymers. The main challenge is the poor adhesion and dispersibility of the NFC in the synthetic or biobased hydrophobic polymer matrices due to the dissimilar nature of the components. In this work we applied Kraft lignin as by product from pulp production for surface modification of commercial NFC to increase the compatibility with polylactic acid (PLA), a biodegradable and bioactive thermoplastic aliphatic polyester. The lignin surface coverage and morphology was determined by scanning electron microscope and potentiometric titration. The hydrophilicity/hydrophobicity effect of adsorbed and polymerized lignin on the 3D printed

composite mechanical properties was also studied. The results indicated increased hydrophobic character of NFC upon lignin surface adsorption and enzymatic polymerization that led to an improved interfacial adhesion with PLA resulting in increased composite mechanical properties (tensile modulus and strength at yield).

Biography

Mojca Božič is an Assistant Professor of Materials in University of Maribor at Faculty of Mechanical Engineering in Slovenia. She has more than 13 years of experience in the field of Material Chemistry (expertise in enzymatic synthesis and bio-catalysis, development of multifunctional biodegradable materials etc.) as well Nanotechnology (expertise in nano-particles synthesis), and surface characterization, modification and their application. She is working on biochemical functionalization and cross-linking of polysaccharide with focus on chitosan and nanocellulose, and biobased-based polymers.

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Yi Liu, Polym Sci, Volume 4
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TUNING STRUCTURE AND ORDERING IN SEMICONDUCTING CONJUGATED POLYMERS

Yi Liu

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Organic semiconductors with tunable optoelectronic properties represent a versatile class of multifunctional materials that can find usages in flexible electronics and energy-related applications. Some fundamental aspects related to their optoelectronic properties are the control of molecular packing, long range ordering, as well as donor-acceptor interfaces, all of which are essential for charge separation and charge transport. Our approaches toward high performance semiconductor materials include (a) developing electroactive building blocks that satisfy bandgap engineering, high absorptivity, and (b) utilizing strong intermolecular interactions to tune chain packing and facilitate charge transport. In this presentation, our recent advances on the development of new electron donors, acceptors and a novel quinoidal unit and their incorporation in conjugated polymers will be discussed. The combination of molecular level understanding of material

composition and control of thin film ordering, offer great opportunity for the development of novel high performance electronic materials.

Biography

Yi Liu is a career Staff Scientist at the Molecular Foundry, Lawrence Berkeley National Laboratory, USA. He obtained his PhD in Chemistry in 2004 from the University of California, Los Angeles, under the direction of Sir J Fraser Stoddart. After finishing his Post-doctoral Research with Professor K Barry Sharpless at the Scripps Research Institute, he joined the Molecular Foundry in 2006 as an Independent Principal Investigator. He is currently the Director of the Organic and Macromolecular Synthesis Facility. His research interests are design and self-assembly of functional organic and organic-inorganic hybrid framework materials, materials chemistry for organic electronics, and fundamental understanding of the associated electronic processes.

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Moonhor Ree et al., Polym Sci, Volume 4
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NEW DIGITAL MEMORY DEVICES FABRICATED WITH DNA AND DNA-MIMICS

Moonhor Ree, Jinseok Lee, Yongjin Kim and Changsub Kim
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We report the first digital nonvolatile memory devices fabricated with DNAs and DNA-mimicking brush polymers. DNA-mimicking brush polymers were newly synthesized based on dielectric brush polyacrylates. Salmon testes and calf thymus DNAs were chosen as natural DNAs. Salmon testes and calf thymus DNA devices, as well as DNA-mimicking brush polymer devices revealed p-type unipolar write-once-read-many-times memory behaviors with low switching-on voltage and high ON/OFF current ratio. Such permanent memory characteristics were confirmed to originate from the charge trapping and hopping nature of nucleobase moieties. Overall, this study demonstrated that DNA and DNA-mimicking

polymers are good candidate materials for the production of p-type permanent memory devices with high performance, high stability and low power consumption.

Biography

Moonhor ree is a professor of polymer science in Pohang University of Science and Technology. He received his M.S from the Korea Advanced Institute of Science and Technology and his PhD in Polymer Chemistry from the University of Massachusetts in 1987. His research interests include polymer synthesis and physics, photon science and its applications in polymers.

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SILVER METALLIZATION AND SELECTIVE METALLIZATION BY SPRAYING ON 3D PRINTED PARTS

Koen Staelens

Jet Metal Technologies, France

Jet metal technologies developed an innovative, green and cost efficient Ag metallization process by spraying two solutions, one oxidant containing the Ag metal salt, the other the reducing agent, (both water based, solvent & CMR & palladium free and REACH compliant) are sprayed simultaneously by using a painting gun at ambient pressure and temperature. The reducing and oxidizing agent start an oxidation-reduction reaction instantly forming a thin, compact, dense and high adherent Ag metal layer on the substrate. This technology can be applied on many substrate geometries (small/big, easy/complex, 2D/3D shape) and basically all substrate material choices, whether it is an electrically conducting or non-conducting surface. The choice of substrates goes from metals over glass, textiles, ceramics, to a long list of plastics (includes many of the plastics used in 3D printing) and composites. The booming use of 3D printed parts in the industry in order to reduce weight & manufacturing costs and shorten lead times, introduces a major challenge in the industry. As the plastic materials used to 3D print components are non-

standard mixtures, basically unique mixes linked to each 3D printer manufacturer, traditional metallization technologies are complex to use. For each 3D printed material, a process needs to be developed to be able to metallize it. By using the jet metal Ag metallization technology to cover completely the 3D printed surface or deposit a 250-300 nm as intermediate conductive Ag layer before plating, this technology offers an easy industrial solution.

Biography

Koen Staelens is a Chemical Engineer graduated from KIRO (Ghent, Belgium) and has been working for the past 15 years in thin film technology (DLC, thermal sprayed coatings, large area sputtering). He has held several positions as Product Manager, Director of Sales, Business Development Manager in different companies (Bekaert Dymonics, Bekaert Advanced Coatings, Soleras Advanced Coatings). His research interests include: metallization, composites and 3D printing.

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NOVEL POLYMER LATEXES BY PHOTOACTIVATED RING-OPENING METATHESIS POLYMERIZATION IN MINIEMULSION VIA THE IN SITU GENERATION OF RUTHENIUM-ARENE CATALYST THROUGH PHOTOLATENT N-HETEROCYCLIC CARBENE LIGAND

Loïc Pichavant¹, Thi Kim Hoang Trinh², David Sauvanier³, Emeline Placet³, Sriprapai Songsee³, Patrick Lacroix-Desmazes³, Jean-Michel Becht², Bassam Tarablsi², Jacques Lalevée², Abraham Chemtob², Julien Pinaud¹ and Valérie Héroguez³

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Many useful polymers as polynorbornene (PNb) or polydicyclopentadiene (PDCPD), having interesting applications as optical components, high impact thermosets or shock absorbers, are prepared by ring-opening metathesis polymerization (ROMP). However, the air sensitivity and the lack of processability of the metal-based catalysts used for ROMP is a drag for their implementation at industrial scale. Nevertheless, *in situ* generation/activation of ROMP catalysts employing stimuli like temperature, pH or UV irradiation can palliate this drawback. Among them, photoactivable ROMP catalysts are certainly the most interesting and have often relied on a ligand dissociation/rearrangement under UV light. In this project, we propose an alternative pathway to generate active ruthenium complexes under UV light. The latter employs photosensitive imidazolium salts to generate N-heterocyclic carbene (NHC) under irradiation that can be subsequently employed as ligands. As such, when associated with the inactive [RuCl₂(p-cymene)]₂ dimer, the system allows the formation of the Noels' catalyst RuCl₂(p-cymene)(NHC) *in situ* under UV light. Polymer latexes, commonly synthesized by emulsion polymerization, have high industrial interest. However, few contributions have been reported regarding polymer latexes obtained by ROMP, first due to the high sensitivity of the active species involved and also because of difficulties to mix ROMP initiators and monomers without causing a premature polymerization. The use of photolatent catalytic systems permit to let go off these drawbacks and can afford a new range of polymer latex by ROMP which cannot be prepared by other routes. In this contribution, the synthesis of PNb by ROMP with two photolatent catalytic systems will be first presented. Then this strategy will be transferred in miniemulsion conditions to prove the ability of this system to form PNb latexes.

Recent Publications

1. Pichavant, L., López-González, M.J., Favereaux, A., Héroguez, V. (2018) Thermosensitive polynorbornene poly(ethylene oxide) nanoparticles loaded with oligoDNAs: An innovative approach for acting on cancer-associated pain. *Polymer Chemistry* 9(3): 362-371

2. Pinaud J., Trinh T.K.H., Sauvanier D., Placet E., Songsee S., Lacroix-Desmazes P., Becht J.M., Tarablsi B., Lalevée J., Pichavant L., Héroguez V., Chemtob A. (2018) *In Situ* Generated Ruthenium-Arene Catalyst for Photoactivated Ring-Opening Metathesis Polymerization Through Photolatent N-Heterocyclic Carbene Ligand. *Chemistry A European Journal* 24(2): 337-341

3. Pichavant, L., Carrié, H., Durrieu, M.C., Héroguez, V. (2016) Nanoparticles highly loaded with gentamicin sulfate by a combination of polyhydroxylated macromonomers and ROMP for the synthesis of bioactive biomaterials. *Polymer Chemistry* 7(45): 7019-7028

4. Cao, E., Pichavant, L., Prouzet, E., Héroguez, V. (2016) The formation and study of poly(ethylene oxide)-poly(norbornene) block-copolymers on the surface of titanium-dioxide particles: A novel approach towards application of si-ROMP to larger surface modification. *Polymer Chemistry* 7(15):2751-2758

5. Pichavant, L., Carrié, H., Nguyen, M.N., Plawinski, L., Durrieu, M.C., Héroguez, V. (2016) Vancomycin Functionalized Nanoparticles for Bactericidal Biomaterial Surfaces. *Biomacromolecules* 17(4):1339-1346

Biography

Loïc Pichavant is a Post-doctoral Researcher at the Laboratoire de Chimie des Polymères Organiques (LCPO) at the University of Bordeaux (France) since 2010. His research interests deal with the formation of nano-objects by ring-opening metathesis polymerization in dispersed media (dispersion; miniemulsion) of cyclo-olefins and their use in biomedical applications (nano-carriers; drug delivery systems). He obtained a PhD Degree in 2009 from the University of Reims Champagnes-Ardennes, working on the synthesis of new biosourced monomers and their polymerization by photoinitiated free radical polymerization.

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Silas Owusu-Nkwantabisah, Polym Sci, Volume 4
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EFFICIENT OPTICAL AND MECHANICAL RESPONSES OF A HYDROPHOBIC ASSOCIATION HYDROGEL

Silas Owusu-Nkwantabisah

Kodak Research Laboratories, USA

Responsive hydrogels are cross-linked soft matter, capable of change in a physical property upon encountering certain stimuli or changes in surrounding conditions. These hydrogels are promising for a wide variety of applications including controlled drug delivery, wound dressings, contact lenses, soft robotics, and tissue engineering. Notwithstanding, some responsive and functional properties compromise the mechanical properties of the hydrogels. Therefore, strategies that produce hydrogels with improved mechanical properties and multiple responses continue to be in high demand despite several advances in the field. Hydrophobic associations, such as dynamic crosslinks, offer a unique strategy to achieve hydrogels with efficient stimuli responses and significant mechanical strength. Moreover, the simple supramolecular interactions within a hydrophobic association hydrogel can produce synergistic effects in the stimuli responsive behavior. This presentation will discuss some of our recent work in designing and creating highly efficient responsive hydrogels

based upon simple supramolecular architectures, such as hydrophobic associations. Such strategies offer benefits including facile preparation of self-healing hydrogels, over 95% enhancement in thermoresponsive light modulation than a conventional system, and a unique soft-stiff thermo-mechanical behavior.

Biography

Silas Owusu-Nkwantabisah is a Research Scientist in the Materials Interfacial Science Department of the Kodak Research Laboratories, Rochester, New York. He received his PhD in Chemistry from the University of Maine under Professor Carl Tripp. Before joining Kodak in 2015, he was a Post-doctoral Associate with Professor Alan Lesser in the Polymer Science and Engineering Department at the University of Massachusetts Amherst. His research interests include responsive polymers, soft matter, surface and colloid chemistry, polymer processing (supercritical CO₂ and melt extrusion), advanced composites and stereolithography.

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March 26-28, 2018
Vienna, AustriaAkil Suzanna, Polym Sci, Volume 4
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POLYMER NANO-STRUCTURING INDUCED ONE-SHOT FABRICATION OF MONODISPERSE GOLD NANOPARTICLES RELEVANT FOR SERS

Akil Suzanna

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Polymer self-assembly has received special attention in the development of nanotechnologies especially for metallic nanoparticles synthesis. In this context, tailoring both nanoparticle shape and size has been intensified recently. Here, we use the vapor-induced phase separation (VIPS) method, which is homopolymer self-assembly to elaborate monodisperse metallic nanomaterials particularly relevant in sensing. To make it possible, a simple deposition of PMMA dispersion, doped with gold precursor onto silicon substrate allows a spontaneous formation of gold nanocubes (GNCs) loaded polymer holes (see Figure 1). To be able to control the structural and optical properties of these nanoparticles, crucial for SERS application, a physico-chemical study of the VIPS process was made. In particular, we investigated the influence of the precursor concentration to obtain monodisperse and uniform nanocubes.

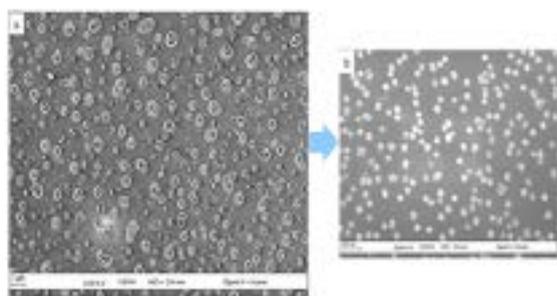


Figure 1: (a) SEM image of gold nanoparticles localized in PMMA nanoholes.

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Biography

Akil Suzanna is an Assistant Professor in the LCP-A2MC, Institut Jean Barriol, Université de Lorraine, Metz, France. Her primary research area is Nanotechnology. She currently develops new methods of fabrication of metallic and semiconductor nanoparticles for the detection of few molecules. She's mainly interested by the elaboration of SERS sensors based on simple and cheap synthesis ways. Her other research interests include nanofabrication, plasmonics, SERS, sensing and semi-conductors.

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DAY 3

Young Research Forum



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Marina F Cosate de Andrade et al., Polym Sci, Volume 4
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LIFE CYCLE ASSESSMENT OF POLY (LACTIC ACID) (PLA): COMPARISON BETWEEN CHEMICAL RECYCLING, MECHANICAL RECYCLING AND COMPOSTING

Marina F Cosate de Andrade¹, Patrícia M S Souza¹, Otávio Cavalett² and Ana R Morales¹

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This work aims to compare different routes of destination for poly(lactic acid) (PLA): chemical recycling, mechanical recycling and composting. Relevant environmental impacts of these alternatives were evaluated using LCA methodology. Composting and hydrolysis lab scale experiments were performed in order to obtain inventory data. Polymerization data in chemical recycling was obtained from computer simulation. Mechanical recycling data from lab scale were combined with the data from a plastics commercial mechanical recycling plant. The SimaPro[®] software was used as a tool to facilitate the LCA implementation. The database used for background processes was Ecoinvent 2.2. Two product systems were considered in this assessment. Restitution product system is based on the idea of restoring residual PLA, and consequently the amount that is not recycled should be produced again through traditional production system. Credit product system is based on the concept of all recycled PLA is a credit in the process, since it replaces PLA produced by traditional route. The different product systems presented similar results. Mechanical recycling showed the lowest environmental impacts, followed by the chemical recycling and composting.

Electricity consumption exhibited the highest impacts between the inputs for chemical and mechanical recycling of PLA. The results are coherent since the recycling alternatives permit to obtain polymer as an output. On the other hand, no polymer is produced in composting, since the final product is only the compost.

Biography

Marina F Cosate de Andrade is a Chemical Engineer (2011) and holds a Master's in Chemical Engineering (2015) from the School of Chemical Engineering (FEQ)/University of Campinas (UNICAMP). Currently, she is a PhD student in Chemical Engineering at the Department of Materials Engineering and Bioprocess (DEMBio) of FEQ/UNICAMP. She has developed projects in mechanical and chemical recycling of poly(lactic acid) (PLA) and its life cycle evaluation (LCA) and PLA polymerization by direct polycondensation using chain extender. Besides, she also worked with 3D printing of PLA and poly(methyl methacrylate) (PMMA) nanocomposites. Her research interests are in the field of Biopolymers, Recycling, Life Cycle Assessment, 3D Printing and Nanocomposites..

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FORMATION AND POLYMERIZATION OF PICKERING EMULSIONS STABILIZED BY MODIFIED CELLULOSE NANOCRYSTALS

Arthur Werner, Gilles Sèbe, Valérie Héroguez and Véronique Schmitt
University of Bordeaux, France

Pickering emulsions are based on amphiphilic particle stabilizers, which adsorb irreversibly at the liquid-liquid interface and form a rigid structure around the droplets. Amongst these particles, cellulose nanocrystals (CNCs) have demonstrated good performances as Pickering stabilizers for oil in water (o/w) emulsions in the presence of salt additives, or after chemical functionalization of the surface. In this work, a wide range of o/w emulsions of monomers were stabilized by amphiphilic modified CNCs. These Pickering emulsions subsequently serve as vessel to perform radical polymerization. In the first system, the CNCs are modified with a non-reactive moiety to tailor the hydrophobic/hydrophilic balance and the polymerization in the droplet is initiated by thermal radical initiator solubilized in the monomer. In the second system, the CNCs are modified with an ATRP initiator, in order to start the polymerization directly from the shell of the droplets to the center of the beads, in a controlled way. In this presentation, we will characterize both the emulsions and the corresponding latexes in a colloidal and polymeric point of view.

Biography

Arthur Werner is pursuing his PhD in Polymer Science at the University of Bordeaux. He obtained his Master's Degree in Physico-Chemistry (2015) and works now under the supervision of Dr. Gilles Sèbe and Dr. Valérie Héroguez. His area of interest is situated at the junction of colloidal and polymer sciences with a specification for Pickering emulsions based on cellulose nanocrystals.

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Recent Publications

1. S.U. Pickering, (1907), CXCVI.—Emulsions, *Journal of Chemical Society*, 91, (0), 2001-2021.
2. I. Kalashnikova, (2012), Modulation of Cellulose Nanocrystals Amphiphilic Properties to Stabilize Oil/Water Interface *Biomacromolecules*, 13, (1), 267-275.
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NANOCELLULOSE – MATERIAL OF THE FUTURE

Ninoslav Ninić¹ and **Matjaž Kunaver²**

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Cellulose is the most widespread natural polymer. If the cellulose structure is reduced to nanometer dimensions and adjusted accordingly in a certain way, its characteristics are remarkably changed. This creates nanocellulose, the most solid material known to humanity. This paper presents the theoretical basis for the production of nanocellulose, its properties and its applicability in several different areas. Nanocellulose is created by means of materials that were practically so far untapped. Nanocellulose is divided into: nanocrystalline cellulose, nanofibrillated cellulose, bacterial cellulose and cellulose-based bionanocomposites. It has exceptional mechanical properties, which mostly indicate the fact that the nanocellulose is five times lighter and five times stronger than steel. It provides a wide applicability in pharmacy, medicine, veterinary medicine, paper, automotive, wood, building, military and other industries. The importance of the use of nanocellulose is also recognized in Slovenia; therefore, six groups have been appointed to deal with this type of problem. Mostly known is group that lead prof. dr. Kunaver, who was more than helpful as co-author.

It is expected that nanocellulose will be used more and more in the future, and we can rightly claim that this is a material of the future.

Biography

Ninoslav Ninić is a Chemical Technology Engineer, currently pursuing his Master's Degree at the Faculty of Polymer Technology in Slovenj Gradec, Slovenia. He graduated from the University of Banja Luka. He has worked for approximately 10 years at BiH in different areas connected with Organic Chemistry Technology. In 2015, he started to work in Paloma, a company with more than 140-year tradition in the manufacturing and marketing of hygienic paper products.

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A. Blanchard et al., Polym Sci, Volume 4
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EFFECT OF HUMIDITY ON MECHANICAL, THERMAL AND BARRIER PROPERTIES OF EVOH FILMS

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Ethylene-vinyl alcohol (EVOH) copolymers are semi-crystalline materials composed of hydrophobic segments of polyethylene (PE) and hydrophilic segments of polyvinyl alcohol (PVOH). Due to its high barrier properties to gases, hydrocarbons and organic vapours at drying state ^[1], EVOH is more and more used in food packaging applications, allowing to extend the life span of the products ^[2]. Nevertheless, the major disadvantage of EVOH is its moisture content sensitivity that causes a significant decrease in the barrier properties in high relative humidity environments ^[3].

The main objective of this study is to get a better understanding of the mechanism of water sorption molecules in these copolymers determining the consequences on the mechanical, thermal, water and oxygen barrier properties. Consequently, these properties were analysed at several water activities (a_w) ranging from 0 to 1 on films elaborated from a 32% ethylene containing copolymer with a crystallinity of 40%.

Water vapour sorption behaviour, corresponding to a BET II sorption isotherm, reveals the sorption of water molecules on polar sites (Langmuir contribution) at low activities and the formation of water clusters at high activities ^[4].

GAB modeled isotherm^[5] combined with the use of the clustering theory from Zimm & Lundberg^[6] underline the existence of a critical activity close to 0,5 corresponding to the presence of one water molecule linked every nine PVOH amorphous units. A strong modification of the properties was observed starting from this critical point, showing how important is the understanding of the water sorption mechanism and the consequences on the properties.

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Biography

A. Blanchard, in the final year of his PhD, his researches taking place at the IMP laboratory (Ingénierie des Matériaux Polymère) at Villeurbanne (France) are focused on a FUI national project in collaboration with several industrial partners (Polyone, Leygatech, Bobino) and scientific centres (CTCPA, CNAM). This project named NOXY II, is dealing with the improvement of the barrier properties of EVOH films for food packaging applications, in order to extend the life span of the products.

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PLA ACTIVE PACKAGING WITH NATURAL ANTIOXIDANTS

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Biopolymers such as PLA have gained a lot of popularity as active packaging, to protect food products from oxidation by the delivery of natural antioxidants, thanks to their ease of thermo-conformation and relatively low price compared to other biopolymers. This research studied the application of PLA active films containing several natural antioxidants into food models to simulate real application of these types of films in food packaging. PLA films were prepared and charged with varying amounts of antioxidants or extracts such as α -tocopherol, gallic acid, red fruits, etc. Films were characterized with FTIR, DSC, TGA and SEM. Active films were applied to different food models to assess their protective action with different methods. Food simulant was used to determine the migration of antioxidants from the film to the food model, and HPLC analyses were performed to quantify results. Oil-in-water (O/W) emulsions with sunflower oil were used as a fatty food model and primary oxidation was measured with peroxide value method. Finally, meat burgers were prepared and covered with active films. Secondary oxidation of burgers was monitored during a month with TBARs method. Results showed that some natural antioxidants improved the thermal stability of prepared films, acting as nucleating agents favoring the crystallization of PLA films. A good inclusion of natural additives in the polymer matrix was proved by the single Tg observed in prepared films. The antioxidant capacity of active films was demonstrated by several tests, which revealed that active films can have strong protection levels.

Biography

Gádor Indra Hidalgo studied a Master's degree in chemical engineering with polymer specialization, and is currently studying a PhD in Polytechnic University of Catalonia (UPC). Her research interests are biopolymers, and polymers for food packaging and she is currently collaborating with industries during industrial trials. Her main research topic is focused on the addition of antioxidants to polymer films to increase lifespan of packaged foods and the sustainability of polymeric packaging solutions.

María Pilar Almajano is a teacher in UPC, specialist in natural antioxidants and has recently started a research path on polymeric active films, its characterization and improvement. Research Interests: Food packaging, biopolymers, multilayer films, new materials.

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POLYIMIDE SYNTHESIS VIA REACTIVE EXTRUSION

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The most common way to synthesize polyimides involves the polycondensation of diamine and dianhydride monomers in solution. The reaction is in general achieved in two steps; first, an intermediate poly(amic acid) is formed, which is further cyclized into polyimide upon appropriate heating. In this solution polymerization process, high boiling temperature solvents are mainly used, such as N-methyl-2-pyrrolidone. As such solvents are hazardous chemicals, there is a real interest to develop an approach preventing their use. To this end, some research works have been recently reported concerning the imidization into an extruder of a poly(amic acid) solution in dichlorobenzene. The drawbacks of this process remain in the solvent elimination and the total reaction time (several hours). In the frame of our project, we developed a method for obtaining polyimides directly in solvent-free conditions via a reactive extrusion process, within typical extrusion residence times (5–10 minutes). Trial runs have been performed on 15 mL micro-compounder. The optimization of the shear conditions and of the reaction temperature allowed obtaining polyimides within a reaction time ranging from 3–5 minutes. The scaling up of this process has been carried out using a twin screw extruder (L/D = 60). The polyimides obtained were characterized by both ¹H and ¹³C NMR. The molar masses of the polyimides were obtained by size-exclusion chromatography. FT-IR spectroscopy has been used to confirm the imide structure and the imidization conversion rate has been determined by DSC.

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Biography

Laurent Verny is a PhD student in the Polymer Materials Engineering Laboratory (IMP) in the Université de Lyon (France). The unit has been divided in to four areas of excellence: Chemistry of Polymers, Structure and Rheology of Polymers: Process and Simulation, Physical Properties and Functional Materials, and Polymers at the Interface of Life Sciences. The IMP laboratory has wide fields of application such as polymers for energy, polymers for the car and aeronautical industries and polymers for medical applications. His research interests include reactive extrusion, polyimide and solvent free synthesis.

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NOVEL MAGNETICALLY CHITOSAN BASED N-HETEROCYCLIC CARBENE AS RECYCLABLE NANOCATALYST AND HIGHLY EFFICIENT FOR CROSS-COUPLING REACTION

Pouria Zarshenas

Shahid Beheshti University, I.R.Iran

In this paper, Novel Magnetically Chitosan@N-Heterocyclic Carbene-Palladium (NHC-Pd) Coated Multi-Walled Carbon Nanotube (MWCNTs) was synthesized in three steps:

1. The reaction of Chitosan, glyoxal and formaldehyde for synthesis of Chitosan@imidazol,
2. Synthesis of magnetic functionalized-MWCNTs and
3. The esterification reaction via the reaction of hydroxyl and carboxylic acid groups of Chitosan@imidazol and magnetic functionalized-MWCNTs respectively, and followed with the attachment of palladium chloride to compose of novel NHC ligand for the first time. Catalytic studies of Magnetic Chitosan@ NHC-Pd Coated MWCNTs for the Suzuki cross-coupling reaction of various aryl halides with aryl boronic acids have been evaluated in the ethanol-water solution. In general, our new catalyst showed superior reactivity for this model reaction. Moreover, the heterogeneous catalyst can be easily recovered by external magnet field and reused for subsequent use without any significant loss in catalytic activity

Biography

Pouria Zarshenas was born in 1994, Tehran-Iran. He started B.Sc in 2013 at Shahid Beheshti University and finished in 2017. He wants continue his academic education in Organic chemistry, the nano particles branch. His research interests are Organic & Inorganic Nano particles research.

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