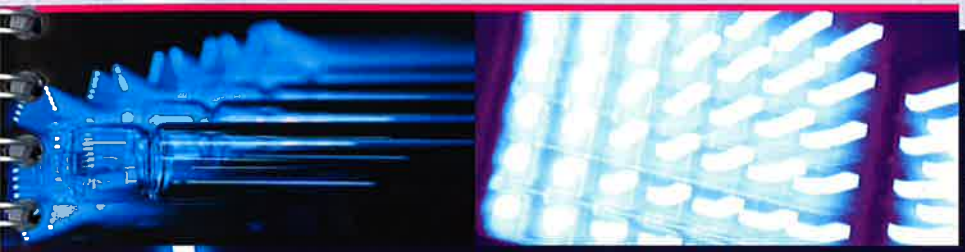
RadTech Europe 13

EUROPE'S EVENT FOR UV/EB CURING

UV/EB – Growing through Innovation



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abstract book

The official event of
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The association for the promotion of UV & EB curing technology

VINCENTZ

Session 1: Advances in photochemistry & polymerization

Title:	1.3	**Storage Stable Thiol-Ene Formulations and Advanced Applications thereof**
Speaker:		Dr Robert Liska, Vienna University of Technology, Austria
Contact:		robert.liska@tuwien.ac.at
Co-Author(s):		Xiaohua Qin, Parichehr Esfandiari, Samuel C. Ligon, Aleksandr Ovsianikov
Abstract:		Thiol-Ene polymerization has gained tremendously increasing interest during the last decade. Advantages such as low oxygen inhibition and shrinkage, uniform networks with significantly improved mechanical properties are accompanied by up to now unsolved disadvantages such as unpleasant odour and poor storage stability. Vinylesters and vinylcarbonates have recently been identified as a promising class of new, low toxic monomers that are not only suitable for biomedical applications but also for classical coatings. The only limitation of moderate reactivity between those of methacrylates and acrylates has been circumvented by thiol-ene polymerization. A new concept in thiol-ene stabilization which gives excellent storage stability with nearly no increase in viscosity within one year will be presented. Generally, monomers could be designed to give material properties similar to that of classical (meth)acrylate-based monomers and oligomers. Finally, advanced applications in the field of 3D printing will be shown.

Session 4: Advances in photochemistry & polymerization II

Title:	4.1	**Elucidating Reaction Mechanisms of Photoinitiators by Magnetic Resonance**
Speaker:		Dr Markus Griesser, Vienna University of Technology, Austria
Contact:		markus.griesser@tuwien.ac.at
Co-Author(s):		Georg Gescheidt, Robert Liska
Abstract:		Photoinitiators play a key role in the UV curing process of e.g. coatings as they have a great impact on reaction speed, conversion and polymer properties. Therefore it is important to understand the initial stages of radical polymerizations. These include not only the properties of the primary radicals, but also follow-up reactions not contributing to chain growth. These aspects of photoinitiated radical reactions can be investigated using magnetic resonance techniques, which are complementary in their results: photo-chemically induced dynamic nuclear polarization (photo-CIDNP) and time-resolved EPR (TR-EPR). As examples of this application, the mechanistic investigation of a diacylgermane system suitable for dental formulations as well other initiators will be presented.

Session 4: Advances in photochemistry & Polymerization

Title:	4.5	**Novel Highly Efficient Initiators for Two-photon Induced Photopolymerization**
Speaker:		Maximilian Tromayer, Vienna University of Technology, Austria
Contact:		maximilian.tromayer@ias.tuwien.ac.at
Co-Author(s):		MAXIMILIAN TROMAYER, ZHIQUAN LI, JAN TORGERSEN, ALIASGHAR AJAMI, ARNULF ROSSPEINTNER, SERGEJ NAUMOV, TOM SCHERZER, ALEKSANDR OVSIANIKOV, ROBERT LISKA
Abstract:		The process of two-photon induced polymerization (TPIP) enables free-form stereolithography with a resolution in the sub-micrometre range, used in the production of scaffolds for tissue engineering, photonic crystals, optical waveguides and microelectronic components. Low achievable writing speeds and lack of highly efficient photoinitiators have been a critical obstruction for further advances in the development of TPIP. Several novel initiators showing good activity even at low laser powers as well as high achievable writing speeds and broad processing windows have been designed. Systematic investigations of structure-activity relationships were conducted via quantum chemical calculations and experimental tests including Z-scan, UV-VIS spectroscopy, TPIP structuring tests and in some cases cytotoxicity assays. Besides achieving writing speeds as high as 5 m/s in the microfabrication of complex 3D structures employing acrylate-based formulations, the latest generation of initiators are synthesized via inexpensive classical C-C coupling reactions like aldol- or knoevenagel-condensation, making them promising candidates for commercialization.

Session 10: Innovations, New Applications

Title:	10.5	**Photocurable P-AMPS-Based Proton Exchange Membranes For Direct Methanol Fuel Cells**
Speaker:		Dr. Samuel Ligon, Vienna University of Technology, Austria
Contact:		samuel.ligon@ias.tuwien.ac.at
Co-Author(s):		Michael Kellner, Philip Radovanovic, Jovan Matovic, Robert Liska
Abstract:		Proton exchange membranes (PEM) for low temperature fuel cells must ensure high proton conductivity and effective separation of anode and cathode under operating conditions. DuPont's sulfonic acid fluoropolymer Nafion has seen commercial success, though high cost limits wider acceptance. As lower cost options, polymers based on 2-acrylamido-2-methylpropane sulfonic acid (AMPS) are also investigated. Swelling of polyAMPS (PAMPS) is however a shortcoming, although this may be reduced by improved crosslinking. Both commercial and novel crosslinkers were tested with AMPS by dissolving with photoinitiator in water and photo-curing. To facilitate conductivity measurements, polymers were constrained within a porous membrane. In contrast to commercial crosslinkers, where high percentages are required to improve conductivity, our new acrylamide based crosslinkers showed excellent results at lower concentrations. Thus 5 wt% crosslinker provided membranes with 2.5 times the conductivity of Nafion. The novel polymers were then coated onto asymmetric membranes increasing proton-conductivity and reducing methanol crossover.

Poster Session

Title	P4	**High-precision manufacturing of 3D hydrogel scaffolds via two-photon polymerization**
Speaker		*Mr. Paul Potzmann*
Contact		paul.potzmann@ias.tuwien.ac.at
Co-Author(s)		*Xiao-Hua Qin, Niklas Pucher, Jan Torgersen, Severin Mühleder, Wolfgang Holnthoner, Heinz Redl, Jürgen Stampfl, Aleksandr Ovsianikov, Robert Liska*
Abstract		Creation of 3D hydrogel scaffolds capable of promoting cell viability and important cell-extracellular matrix (ECM) interactions is critical for tissue engineering applications. To mimic the biochemical and structural complexities of ECM, two-photon polymerization (2PP) shows the greatest promise because it allows the fabrication of user-dictated shapes with micrometer-scale resolution. Poly(ethylene glycol) diacrylates have been widely used as hydrogel precursors in the biomaterials community due to their high reactivity. However, the residues of acrylate groups are potentially cytotoxic. We previously proved that vinyl esters (VEs) are much less cytotoxic than their (meth)acrylates references. Although VEs are generally not as reactive as acrylates, the thiol-vinyl ester click reactions are robust enough for 2PP microfabrication of hydrogels. In this work, we present the synthesis of gelatin vinyl esters, bovine serum albumin based macrothiols, and microfabrication of protein-based hydrogels via two-photon-excited thiol-vinyl ester photopolymerizations.

Poster Session

Title	**P5**	**Developing anti-oxygen inhibition strategies for LED-based wood coatings**
Speaker		*Dr Samuel Ligon*
Contact		samuel.ligon@ias.tuwien.ac.at
Co-Author(s)		*Branislav Husár, Harald Wutzel, Helmuth Hoffmann, Jan Torgersen, Robert Liska*
Abstract		Light emitting diodes (LEDs) are becoming increasingly popular in photo-curing applications as alternatives to Hg lamps. Matching photoinitiator absorbance with frequency of the LED source is one important consideration. For wood coatings photo-cured in open air, an additional difficulty is encountered since molecular oxygen inhibits radical polymerization. This leads to insufficiently cured films that remain tacky at the surface. Although nitrogen-inerting can be highly successful in providing proper cure, the method is impractical for many SME end users. Chemical additives which combat oxygen inhibition are preferred instead. A variety of additives have been introduced in the scientific and patent literature, which we have chosen to experimentally reinvestigate for LED based curing. Bulk cure was monitored by transmission IR and surface cure by ATR. Coupling of the RT-IR with the LED power source through a multichannel relay trigger improves precision for investigating the importance of wavelength and intensity on cure.

Poster Session

Title	**P6**	**Insights into the Reactivity of Benzaldoxime Esters as Photoinitiators**
Speaker		*Dr Markus Griesser*
Contact		markus.griesser@tuwien.ac.at
Co-Author(s)		*Arnulf Rosspeintner, Claudia Dworak, Georg Gescheidt, Robert Liska*
Abstract		Photoinitiators are key compounds in light curable polymerization systems by generating the reactive (radical) species. A novel initiating system, comprising a benzaldoxime ester and a sensitizer displays an excellent efficiency. The mechanism of the photoinduced reactivity of this initiating system was investigated using a combined effort of time resolved EPR (TR-EPR), chemically induced dynamic nuclear polarization (photo-CIDNP) spectroscopy and photo-DSC. The combination of these techniques offers conclusive and consistent insights into the reaction sequence of the photoinitiating system and the subsequent reactivity towards acrylate monomers. Thus information on the photophysical basis and the chemical nature of the active species can be elucidated. Furthermore as the initiator generates CO2 during cleavage the effect of oxygen inhibition has been studied. Benzophenone has proven to be a very effective sensitizer and is acting via the triplet state, greatly enhancing the light harvesting process compared to the pure benzaldoxime ester or other sensitizers.

Poster Session

Title	P7	**Vinyl carbonates with improved mechanical properties**
Speaker		*Mr. Maximilian Tromayer*
Contact		maximilian.tromayer@ias.tuwien.ac.at
Co-Author(s)		*Maximilian Tromayer, Andreas Mautner, Branislav Husár1, Christian Heller, Franz Varga, Thomas Koch, Karin MacFelda, Günter Russmüller, Jürgen Stampfl, Robert Liska*
Abstract		The fabrication of 3D scaffolds by lithography-based additive manufacturing technology (AMT) represents an appealing approach in bone tissue engineering. In this contribution, (meth)acrylate-based monomers were replaced by vinyl carbonates with 1-3 orders of magnitude lower cytotoxicity. Although the photoreactivity is lower than those of acrylates, they are sufficiently photoreactive to be structured by lithography based AMT. By addition of thiols to the photocurable formulation, curing speed can reach the value for acrylates. The mechanical properties and rates of degradation can be tuned over a broad range. All polymers were significantly stiffer than polycaprolactone, being almost as stiff as poly(lactic acid) (PLA). Dianhydro-D-glucitol divinyl carbonate outperforms PLA due to its rigid spacer. Degradation of the polymers results in the formation of non-toxic degradation products of low molecular weight that can be easily transported within the human body. In vivo testing proved an excellent biocompatibility of these materials.

Poster Session

Title	**P8**	**Development of a novel photocurable hydrogel precursor: hyaluronan vinyl esters**
Speaker		*Mr. Paul Potzmann*
Contact		paul.potzmann@ias.tuwien.ac.at
Co-Author(s)		*Xiao-Hua Qin, Severin Mühleder, Wolfgang Holnthoner, Heinz Redl, Jürgen Stampfl, Aleksandr Ovsianikov, Robert Liska*
Abstract		Hyaluronan vinyl esters (HAVE), a novel biocompatible and photocurable hydrogel precursor, were synthesized via lipase-catalyzed transesterification reaction. By tuning reaction time and stoichiometry, degree of substitution could be controlled within a wide range. In-situ photorheology was used to monitor the curing and enzymatic degradation kinetics of HAVE hydrogels. It was found that the photoreactivity of HAVE towards homopolymerization increased with higher degree of substitution. More importantly, the thiol-ene click chemistry was able to improve the photoreactivity of HAVE. Additionally, the control over the concentration of HAVE as well as the crosslinking density provided hydrogels with a wide range of gel stiffness. MTT assay of both HAVE solutions and extracts of HAVE pellets proved that HAVE has negligible cytotoxicity and therefore promising for potential biomedical applications.